PB88-133616

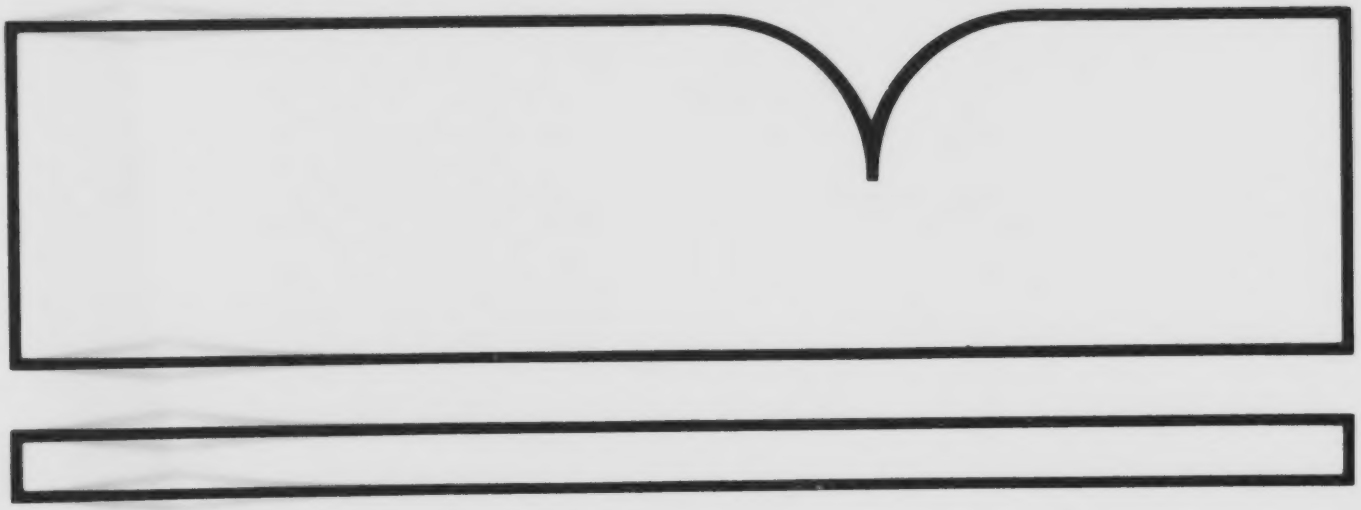
Chemical Characterization of Polynuclear Aromatic Hydrocarbon Degradation Products from Sampling Artifacts

Battelle Columbus Div., OH

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Dec 87



U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-133616

EPA/600/4-87/039
December 1987

CHEMICAL CHARACTERIZATION OF POLYNUCLEAR AROMATIC HYDROCARBON DEGRADATION PRODUCTS FROM SAMPLING ARTIFACTS

by

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Contract Number: 68-02-4127

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/4-87/039	2.	3. RECIPIENT'S ACCESSION NO. PB88 133616/AS
4. TITLE AND SUBTITLE Chemical Characterization of Polynuclear Aromatic Hydrocarbon Degradation Products from Sampling Artifacts		5. REPORT DATE December 1987 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. C. Chuang, S. W. Hannan and L. E. Slivon		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Columbus Division 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final - 9/15/86 - 7/31/87 14. SPONSORING AGENCY CODE EPA-600/08
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

The objective of this study was to characterize the polar components, mainly polynuclear aromatic hydrocarbon (PAH) derivatives, in air samples and to determine whether these compounds are from sampling artifacts or from the sampled air. A literature survey was conducted to review the studies about polar PAH derivatives found in the air. In general, there is limited chemical and biological information for polar PAH available in the literature. The polar fractions of air samples did show a significant amount of mutagenic activity. More studies are needed in this area to determine the polar components responsible for the activity. Some reactive PAH including acenaphthylene and cyclopenta[c,d]-pyrene partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides after storage for 30 days in the dark at room temperature between sampling and extraction. The NCI GC/MS method is a very sensitive technique for the determination of NO_2-PAH and oxygenated PAH (OXY-PAH), however, analyses of the standards are required to confirm the identification. The NCI and PCI MS/MS techniques can provide characteristic fragmentation patterns for NO_2-PAH and OXY-PAH respectively. More studies are needed to evaluate a fast screening method to determine these compounds with MS/MS.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 76 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

Measurement and monitoring research efforts are designated to anticipate environmental problems, to support regulatory actions by developing an indepth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The chemical characterization of polynuclear aromatic hydrocarbon degradation products from sampling artifacts provides important information that can be applied to the measurement of the extent of human exposure to the polynuclear aromatic compounds.

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ABSTRACT

The objective of this study was to characterize the polar components, mainly polynuclear aromatic hydrocarbon (PAH) derivatives, in air samples and to determine whether these compounds are from sampling artifacts or from the sampled air.

A literature survey was conducted to review the studies about polar PAH derivatives found in the air. In general, there is limited chemical and biological information for polar PAH available in the literature. Most of the studies revealed that PAH and NO_2-PAH cannot totally account for indirect- and direct- acting mutagenicity in air samples. The polar fractions of air samples did show a significant amount of mutagenic activity. We concluded that more studies are needed in this area to determine the polar components responsible for the activity.

A storage stability study of PAH collected on quartz fiber filters and XAD-2 resin was conducted. The results showed that some reactive PAH including acenaphthylene and cyclopenta[c,d]pyrene partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides after storage for 30 days in the dark at room temperature between sampling and extraction.

The determination of unknown polar components in air samples is a complex task. The NCI GC/MS method is a very sensitive technique for the determination of NO_2-PAH and oxygenated PAH (OXY-PAH), however, analyses of the standards are required to confirm the identification. The NCI and PCI MS/MS techniques can provide characteristic fragmentation patterns for NO_2-PAH and OXY-PAH respectively. More studies are needed to evaluate a fast screening method to determine these compounds with MS/MS.

This report was submitted in fulfillment of Contract No. 68-02-4127 conducted by Battelle Columbus Division under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period of September 15, 1986 to July 31, 1987. The work was completed as of July 31, 1987.

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ACKNOWLEDGEMENT

The financial support of the U.S. Environmental Protection Agency and the thoughtful discussions of Dr. Nancy K. Wilson are gratefully acknowledged.

SECTION 1

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) have been extensively studied in recent years and have received increasing attention in the investigation of air pollution. Many PAH are known to be animal carcinogens, mutagens, or both. Most PAH are likely to react with air, sunlight, and other pollutants (O_3, NO_x and SO_2) in the atmosphere to form PAH derivatives because PAH can absorb light at the wavelengths found in sunlight (>300 nm). The PAH derivatives present in air arise partly from various combustion emissions sources, in addition to atmospheric transformation. Degradation products of PAH may also be formed as artifacts of sample handling or sample storage conditions. Recently, Battelle conducted a study which showed that the amount of particle-bound cyclopenta[c,d]pyrene decomposes to about half of its original value after storage for 30 days in the dark at room temperature. In general, little is known about the PAH degradation products formed as sampling artifacts. However, it has been demonstrated that PAH degradation products may exhibit a higher mutagenic activity than their parent PAH. Therefore, it is important to determine whether those PAH derivatives are sampling artifacts or were actually present in the air sampled.

Many studies have demonstrated that PAH and NO_2-PAH cannot totally account for the indirect- and direct-acting mutagenicity of air samples; other classes of compounds must also contribute to the activity. In fact, the polar fractions of air samples have shown very strong direct-acting mutagenicity. In some cases the activity of the polar fraction is greater than 50 percent of the total activity. We expect that many of the PAH derivatives, such as NO_2-PAH and oxygenated PAH (OXY-PAH), are present in the polar fractions. However, only limited biological and chemical information is available for these polar components in the air. Therefore, a study was carried out to characterize PAH degradation products in air.

The objective of this study was to characterize the polar components, mainly PAH derivatives, in air samples and to determine whether these compounds are sampling artifacts or are from the sampled air. This study consisted of the following subtasks:

1. Conducting a literature survey to review the studies about polar PAH derivatives found in the air,

2. Performing a storage stability study of PAH collected on quart fiber filters and XAD-2 resin,

3. Conducting chemical characterization of the day-0 and day-30 samples in an attempt to determine the PAH degradation products produced due to storage, and

4. Preparing the samples from the stability study for bioassay.

SECTION 2

CONCLUSIONS

The results of the literature survey showed that there is limited chemical and biological information on PAH derivatives in air with the exception of NO_2-PAH. Most of the studies indicated that PAH and NO_2-PAH cannot totally account for indirect-and direct-acting mutagenic activity. The polar fraction of air samples did show a significant portion of mutagenic activity. It is concluded that more studies are needed in this area to determine the polar components responsible for the mutagenicity.

The results of the storage stability study showed that the reactive PAH, acenaphthylene and cyclopenta[c,d]pyrene, partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides after storage before extraction for 30 days in the dark at room temperature. One of the degradation products, pyrene-3,4-dicarboxylic acid anhydride, has been reported to be a direct-acting mutagen. Therefore, future air sampling studies should involve a minimum of sample handling and storage to reduce the degradation of reactive PAH.

The determination of unknown polar components in air samples is a complex task. The EI GC/MS analyses of the unfractionated filter samples did not detect PAH derivatives. Even though the NCI GC/MS method is a very sensitive method for the determination of NO_2-PAH and OXY-PAH, the analyses of standards are required to confirm the identification. In most cases, the identification of polar PAH derivatives from the NCI GC/MS method is only tentative. We conclude that more investigation, such as fractionation of the sample and evaluating different analytical methods, is needed to characterize the polar components in air samples.

SECTION 3

RECOMMENDATIONS

The following recommendations are based on the results of this study:

1. A study should be performed to investigate the chemical and biological characteristics of a series of reactive PAH and their degradation products and to estimate the extent of mutagenic activity of PAH degradation products from sampling artifacts.

2. A study should be performed to evaluate a fast screening method to determine NO_2-PAH and OXY-PAH by using MS/MS.

3. A study should be performed to characterize polar components in air samples by fractionation to enrich the polar fraction and by using a combination of different analytical tools to determine the polar components.

SECTION 4

EXPERIMENTAL PROCEDURES

LITERATURE SURVEY

A literature survey was performed by a computer search of five data bases:

Data Base	Years Searched
Chemical Abstracts	1967 - 1986
APTIC	1966 - 1978
NTIS	1970 - 1986
Medline	1970 - 1986
Cancerline	1970 - 1986

Over 100 citations were obtained as a result of the computer search. Abstracts or citations considered most relevant to the subject area were reviewed and divided into two subsets: analytical and biological data, for further evaluation. Photocopies of some important articles were also obtained to allow a more detailed evaluation.

STORAGE STABILITY STUDY

Two sets of four modified medium volume samplers (modified General Metals PS-1 samplers with General Metals bypass motors) were employed in the ambient air sampling. Samplers were placed on the ground in an open space in the Battelle parking lot. The two sets of four samplers were separated from each other by about 2 ft. The four samplers of each set were separated from each other by about 1 ft. The sampling was conducted on weekends to

reduce the contribution of local vehicle exhaust emissions to the samples. A 5-ft exhaust hose leading away from the sample module was attached to each sampler. Quartz fiber filters and XAD-2 traps in series were used to collect particles and vapors. Prior to sampling, each sampler was calibrated using a Dry Gas Meter (Rockwell Model 415) to obtain a flow rate of 6.7 cfm. Flow measurements from the sampler Magnehelic gauge were then recorded. The sample module was then placed on the sampler, and adjustment was made using an orifice calibrator to obtain the same calibrated reading on the Magnehelic gauge. Ambient air was sampled for 24 hours at 6.7 cfm. The flow was checked approximately every 6 hr and maintained at 6.7 cfm throughout the sampling period. The ambient temperature during sampling ranged from 69° to 86° °F.

The XAD-2 and filter samples were stored as replicate pairs in the dark at room temperature for 0-, 10-, 20-, and 30- day intervals before extraction. The XAD-2 and filter samples were extracted separately with dichloromethane for 16 hr after each storage period. Sample extracts were concentrated to 1 ml using Kuderna-Danish (K-D) evaporation. An aliquot of each extract was removed for residue weight measurement. The remaining extract of each sample was divided into two equal portions. Portion I was used for chemical analysis and portion II was used for bioassay analysis.

Portion I of the replicate pairs from XAD-2 samples were combined and fractionated into four fractions with open-bed silica gel column chromatography. The silica gel column (~0.55 cm I.D. x 7 cm in a 15 cm disposable Pasteur pipette) was packed with 1 g of 5 percent H_2O-deactivated silica gel in hexane, and the gel was retained with a glass wool plug. The sample extract was solvent-exchanged into hexane and was then applied to the column. The elution solvents were applied to the column in the following sequence: 2.5 ml of hexane, 4 ml of benzene, 4 ml of dichloromethane, and 4 ml of methanol. Each fraction was concentrated to 1 ml by K-D evaporation for analysis. The replicate pairs of each filter sample were combined, but not fractionated by silica gel chromatography, since only about 1 mg of organic extractable mass was available in each combined filter sample.

SAMPLE PREPARATION FOR MICROBIOASSAY ANALYSIS

Portion II of each filter and XAD-2 sample was diluted with dichloromethane to the extracts that a 1 ml aliquot represented. 62.5 m^3 and 6.25m^3 respectively with dichloromethane. The conditions for sample dose levels are summarized in Table 1. Based on the required dose levels, aliquots of the diluted extract were removed to clean sample vials and evaporated to near dryness under a gentle nitrogen stream. A 2 μl aliquot of dimethylsulfoxide (DMSO) was added to each sample vial. The DMSO samples were mixed with a Vortex mixer and evaporated under nitrogen for an additional 5 min to evaporate all of the dichloromethane. The sample vials were sealed with screw caps and immediately stored under dry ice. The samples were packed in dry ice and sent to EPA/HERL for microbioassay.

TABLE 1. DOSE LEVELS OF FILTER AND XAD-2 SAMPLES FOR MICROBIOASSAY

Sample Code	Dose Level, m^3/vial (a)
Filter Day 0 - 1	1, 2, 5, 10, 20
Filter Day 0 - 2	1, 2, 5, 10, 20
Filter Day 10 - 1	1, 2, 5, 10, 20
Filter Day 10 - 2	1, 2, 5, 10, 20
Filter Day 20 - 1	2, 2, 5, 10, 20
Filter Day 20 - 2	1, 2, 5, 10, 20
Filter Day 30 - 1	1, 2, 5, 10, 20
Filter Day 30 - 2	1, 2, 5, 10, 20
Filter Field Blank	normalized 1, 2, 5, 10, 20
XAD-2 Day 0 - 1	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 0 - 2	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 10 - 1	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 10 - 2	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 20 - 1	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 20 - 2	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 30 - 1	0.1, 0.2, 0.5, 1, 2
XAD-2 Day 30 - 2	0.1, 0.2, 0.5, 1, 2
XAD-2 Field Blank	normalized 0.1, 0.2, 0.5, 1, 2

(a) m^3/vial represents the equivalent volume of sampled air.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) ANALYSIS

The unfractionated extracts of filter samples and the aromatic fractions of the XAD-2 samples were analyzed by electron impact (EI) and negative chemical ionization (NCI) GC/MS in the multiple ion detection (MID) mode to determine PAH and NO_2-PAH quantitatively. The selected filter extracts and XAD-2 fractions were also analyzed by EI and NCI GC/MS in the full mass scan mode to determine the unknown components qualitatively. A Finnigan 4500 GC/MS was used for these analyses. Methane was used as the GC carrier gas and the NCI reagent gas. An Ultra #2 fused silica capillary column was used for analyte separation, and the outlet GC column was located at the inlet of the MS ion source. Data acquisition and processing were performed with a Finnigan INCOS 2300 data system. The GC and MS operating conditions are listed in Table 2.

In the quantitative MID analysis, the identification of PAH and NO_2 PAH was based on the GC retention time of the respective molecular ion relative to the internal standards (9-phenylanthracene for PAH and Dg-1-nitropyrene for NO_2-PAH). The quantification was based on comparisons of the respective integrated ion current responses for the monitored molecular ions to the internal standard. The response factor for each target compound relative to the respective internal standard was determined from the standard analyses. The following equation was used for quantification:

$$C_S = \frac{A_S \times C_{is}}{A_{is} \times R_f}$$

$$T_S = \frac{C_S \times FV \times F}{V}$$

where:

C_S = Concentration of a target compound in the extract, ng/μl

A_S = Molecular ion area of a target compound

C_{is} = Concentration of the internal standard, ng/μl

A_{is} = Molecular ion area of the internal standard

R_f = Response factor of a target compound

T_s = Concentration of a target compound in the air, ng/m^3

FV = Final volume of the extract analyzed, μl

V = Total volume of air sampled, m^3

F = Factor for the correction of the portion of the extract analyzed.

The individual standard dichloromethane solutions of acenaphthylene and cyclopenta[c,d]pyrene were spiked evenly onto the quartz fiber filters and were exposed to ultraviolet light for four days to obtain the mixtures of parent PAH and the corresponding PAH degradation products, PAH dicarboxylic acid anhydride. The exposed standard solutions were analyzed by EI and NCI GC/MS in the full scan mode.

In the qualitative full mass scan EI GC/MS analysis, tentative identifications were based on manual interpretation of the of the background-corrected mass spectra assisted by on-line library search. The library search data base was the most recently available EPA/NIH mass spectral data base containing in excess of 42,000 unique reference spectra. The tentative identifications of the NCI spectra were based on manual interpretation of the mass spectra and the retention times of compounds (where standards were available) relative to the internal standard D9-1-nitropyrene.

TRIPLE QUADRUPOLE MASS SPECTROMETRY (TSQ) ANALYSIS

A Finnigan triple quadrupole mass spectrometer (TSQ) equipped with a Finnigan GC was used to determine the daughter spectra of selected standards. The MS was operated in positive chemical ionization (PCI) and NCI modes. Each of the two mass analyzers were independently mass-calibrated using perfluorotributylamine (FC-43). The MS was tuned to optimize the daughter ion spectrum of m/z 219 from FC-43 when the PCI mode was employed. With the NCI condition, the MS was tuned to optimized the

daughter ion spectrum of m/z 595 from FC-43. The collision energy was 25 eV and the collision gas pressure was 6×10^{-4} torr of argon. The data acquisition and processing was performed by using the System Status (SS) software program.

Standard solutions and sample extracts were introduced into the ion source through either the solid probe or the GC column. The first mass filter (Q1) was set at the specific protonated molecular ion or molecular ion while the third quadrupole was at full mass scan mode resulting in the daughter spectrum from the selected parent ion of Q1. The Q3 mass scan range was from 10 amu to M amu at 1 sec; M denotes the molecular ion monitored at Q1. If the GC separation was employed prior to MS/MS analysis, the GC column and temperature program were the same as the normal GC/MS analysis described in Table 2.

The NCI daughter spectra of NO_2-PAH revealed specific patterns which are M^-, $(M-NO)^-$ and $(NO_2)^-$. Thus, a specific parent/daughter ion transition was selected in single ion monitoring (SIM) mode, a technique analogous to SIM in GC/MS in an attempt to increase the detection specificity and signal-to-noise. The standards of selected NO_2-PAH and hydroxy nitropyrenes were analyzed under this condition. The filter extract and XAD-2 fractions were also analyzed by NCI GC/MS/MS in an attempt to determine the daughter spectra of a few nitrogen-containing compounds tentatively identified from the NCI/GC/MS method, using the specific parent/daughter ion transition mode.

TABLE 2. THE EI AND NCI GC/MS OPERATING CONDITIONS

Chromatography	
Column:	Ultra #2 crosslinked, 50% phenylmethyl silicone 50m x 0.32mm, 0.5μ film thickness
Carrier:	Methane
Carrier Linear Flow Velocity:	~50 cm/sec at 200°C
Injection Volume:	1 μl for on-column injection 2 μl for splitless injection
Injection Mode:	On-column mode for NCI Splitless mode for EI
Temperature Program	
Initial Column Temperature:	40°C
Initial Hold Time:	1 min.
Program Rate:	100°C (3 min.) to 300°C at 8°C/min.
Final Hold Time:	15 min.
Mass Spectrometer	
Ionization:	EI at 70 eV, NCI at 150 eV
Filament Emission Current	0.35 ma
Ionizer Temperature:	180°C
Electron Multiplier gain:	~10^5 gain

SECTION 5

RESULTS AND DISCUSSION

LITERATURE SURVEY OF POLAR PAH DERIVATIVES IN AIR

Many studies have shown that air particulate matter contains extractable organic matter that exhibits mutagenic and carcinogenic activity (1-10). Pott's group (2-3) demonstrated that PAH with greater than four rings accounted for significant amounts of the carcinogenic potency of air particulate extracts. However, the polar fractions containing PAH derivatives were also carcinogenic to some extent. The authors pointed out that more studies are needed to characterize these polar compounds.

Polynuclear aromatic hydrocarbon (PAH) in air have been extensively studied in recent years. Many studies have demonstrated that PAH cannot totally account for mutagenic activity; other classes of compounds must also contribute to the activity. Indeed, the polar fractions of air particulate extracts have revealed direct-acting mutagenic activity (8-12). In some cases the activity was greater than 50 percent of the total activity. Recently, members of one class of PAH derivatives, nitro-PAH (NO_2-PAH) such as 1-nitropyrene, 2-nitrofluoranthene, and dinitropyrenes, which are strong direct-acting mutagens, were shown to be present in air samples (13-15). Another class of PAH derivatives having direct-acting activity, hydroxy-nitro-PAH (OH-NO_2-PAH), was also identified in air particulate extracts (16). One study has demonstrated that the mutagenicity of OH-NO_2-pyrene isomers ranged from less than 0.1 to 8 times the activity of 1-nitropyrene (17). Nevertheless, NO_2-PAH and OH-NO_2-PAH cannot totally contribute to the mutagenicity in the polar fractions; other classes of compounds, such as oxygenated PAH (OXY-PAH) may also account for the activity.

The OXY-PAH have been found in various environmental samples, such as diesel exhaust particulate and air particulate matter (18-23). Studies have demonstrated that polar fractions containing OXY-PAH exhibited direct-acting

mutagenicity (18, 21). However, it is not clear whether these OXY-PAH account for the majority of the mutagenicity. Only a few OXY-PAH, such as benzo[a]pyrene quinones and pyrene-3,4-dicarboxylic acid anhydride, were reported to have direct-acting activity (24,25). Overall, there is a lack of mutagenicity and carcinogenicity data on individual OXY-PAH in the literature, and more research should direct to studies of the biological activity of OXY-PAH.

Analytical methods including EI and CI GC/MS or HPLC have been used to determine polar PAH including NO_2-PAH and OXY-PAH. The analytical methods to determine NO_2-PAH have been well established compared to methods for other polar PAH in recent years (26). No systematic efforts have been made to determine OXY-PAH. In most cases, isomer-specific identification of OXY-PAH was not possible by GC/MS alone. A combination of GC/MS with ultraviolet (UV) or fluorescence spectrometry was used to determine isomeric OXY-PAH. Furthermore, the absence of authentic standards has prevented the positive identification of isomeric OXY-PAH. Some isomeric compounds have quite different biological activity. For instance, phenalen-1-one is a potent mutagen and is toxic to microalgae, but its isomer fluorene-9-one is not active as a bacterial mutagen (28-29). Thus, the ability to determine specific isomeric compounds is important, and more investigations are needed.

Identification of the unknown mutagens or carcinogens present in air is a very complex task. A new technical approach, bioassay-directed fractionation and characterization has been demonstrated to be an effective approach to determine mutagenicity of fractions of complex mixtures such as diesel exhaust particulate matter and air particulate matter (30). In the future, bioassay-directed fractionation and characterization may be a valuable tool for the investigation of the compounds responsible for the mutagenicity of air.

DETERMINATION OF PAH AND NO_2-PAH IN XAD-2 AND FILTER SAMPLES

The filter extracts and aromatic fractions of XAD-2 samples from the storage stability study were analyzed by GC/MS to determine selected PAH and NO_2-PAH. The concentrations of each target PAH and NO_2-PAH detected in XAD-

2 and filter samples were calculated as ng/m^3 and are summarized in Tables 3 and 4 respectively.

Based on our previous experience with these parallel sampling and analysis procedures, a variance of about 20 percent for identical samples is to be expected. Thus, the PAH vapors collected on XAD-2 resin appear to be stable over the 30-day storage except that one reactive PAH, acenaphthylene, showed a slightly decreasing concentration trend. This reactive PAH not detected on any of the quartz fiber filters. The non-detection of acenaphthylene on filters may be due to its degradation to below the detection limit (~0.05 ng/m^3), since this compound was relatively volatile and was mainly captured on XAD-2 resin. The results also showed that most particle-bound PAH, except for cyclopenta[c,d]pyrene were not adversely influenced by a 30 day storage time. This finding agrees with the results from the previous stability study (31). The levels of cyclopenta[c,d]pyrene decreased from 0.35 ng/m^3 to 0.17 ng/m^3 after 30 days storage. The low levels of cyclopenta[c,d]pyrene adsorbed on the XAD-2 resin prevented any firm stability conclusion. However, the data are consistent with a decreasing trend with storage time. Both acenaphthylene and cyclopenta[c,d]pyrene, having similar structure with vinylic bridges, are reactive PAH and can be expected to show storage instability over 30 days. The increased chemical reactivity of the relatively localized double bond found in these compounds apparently make them susceptible to oxidation. The degradation products of these PAH are discussed in a later section.

With the exception of 2/3-NO_2-fluoranthene, storage losses of vapor and particle-bound NO_2-PAH were insignificant. As shown in Table 4, nitro-naphthalene, nitro-anthracene/phenanthrene and nitro-pyrene did not show any decreasing concentration trend. The calculated concentration of 2/3-nitrofluoranthene decreased from 0.026 ng/m^3 to 0.015 ng/m^3 after storage for 30 days. As expected, the levels of NO_2-PAH found in air were much lower than that of their parent PAH.

The distributions of PAH between the filter and XAD-2 resin from this stability study were as follows: 2-ring PAH, >99 percent on XAD-2; 3-ring PAH, 99 percent on XAD-2; 4-ring PAH, 95 percent on XAD-2 for pyrene, and fluoranthene, and 40 percent on XAD-2 for benz[a]anthracene and chrysene; 5-

TABLE 3. CONCENTRATIONS OF PAH FOUND IN XAD-2 AND FILTER SAMPLES AS A FUNCTION OF STORAGE TIME

Compound	Concentration, ng/m3(a)							
	Storage time between sampling and extraction, Days							
	0		10		20		30	
Naphthalene(b)	0.30	>200	0.23	>230	0.39	>220	0.25	>200
Acenaphthylene	ND(c)	7.2	ND	5.3	ND	6.2	ND	6.2
Acenaphthylene dihydro	0.14	34	0.10	31	0.10	34	0.12	27
Fluorene	0.13	38	0.12	32	0.17	34	0.18	30
Phenanthrene	1.1	130	1.0	120	1.3	140	1.3	120
Anthracene	0.12	3.6	0.10	3.3	0.10	3.9	0.10	3.2
Fluoranthene	0.91	29	1.1	26	1.1	31	0.99	28
Pyrene	0.59	14	0.65	13	0.66	16	0.66	17
Cyclopenta[c,d] pyrene	0.35	0.13	0.22	0.14	0.17	0.09	0.17	0.11
Benz[a]anthracene	0.22	0.15	0.22	0.14	0.23	0.16	0.25	0.15
Chrysene	0.60	0.48	0.71	0.55	0.69	0.47	0.63	0.49
Benzofluoranthenes	0.77	ND	0.74	ND	0.70	ND	0.77	ND
Benzo[e]pyrene	0.33	ND	0.35	ND	0.33	ND	0.38	ND
Benzo[a]pyrene	0.26	ND	0.27	ND	0.24	ND	0.26	ND
Indeno[1,2,3-c,d] pyrene	0.29	ND	0.29	ND	0.33	ND	0.33	ND
Benzo[g,h,i] perylene	0.53	ND	0.56	ND	0.52	ND	0.56	ND
Coronene	0.42	ND	0.39	ND	0.35	ND	0.43	ND

(a) The first number is for the filter samples; the second number is for the corresponding XAD-2 samples.

(b) The naphthalene peak was saturated in each XAD-2 sample, thus the values are reported as greater than the calculated value.

(c) ND: not detected.

TABLE 4. CONCENTRATIONS OF NO_2-PAH FOUND IN XAD-2 AND FILTER SAMPLES AS A FUNCTION OF STORAGE TIME

Compound	Concentration, ng/m3(a)							
	Storage time between sampling and extraction, days							
	0		10		20		30	
9-nitroanthracene	0.077	0.21	0.080	0.27	0.091	0.24	0.082	0.28
2/3-nitro-fluoranthene	0.026	ND(b)	0.026	ND	0.021	ND	0.015	ND
1-nitropyrene	0.009	ND	0.010	ND	0.011	ND	0.010	ND
1,3-dinitropyrene	ND	ND	ND	ND	ND	ND	ND	ND
1,6-dinitropyrene	ND	ND	ND	ND	ND	ND	ND	ND
1,8-dinitropyrene	ND	ND	ND	ND	ND	ND	ND	ND

(a) The first number is for the filter samples; the second number is for the corresponding XAD-2 samples.

(b) ND: not detected.

ring PAH, 25 percent on XAD-2; 6- to 7-ring PAH, 100 percent on filters. Approximately 10 to 20 percent more PAH vapors were collected on XAD-2 resin compared to those collected in the previous study (31). The difference may be due to ambient sampling temperature, which was 20°F higher than that in the previous study. The higher temperature may decrease the collection efficiency of PAH on prefilters. Thus relatively more PAH were collected on the back-up XAD-2 trap. Overall, the results from both stability studies all indicated that there is a breakthrough of 2- to 5-ring PAH from the prefilters during medium volume sampling conditions. The use of back-up adsorbents is essential for quantitative determination of PAH in air.

DETERMINATION OF PAH DERIVATIVES IN XAD-2 AND FILTER SAMPLES

The day-zero and day-thirty filter extracts and selected XAD-2 fractions were analyzed by EI and NCI GC/MS in the full mass scan mode to determine the unknown components. The tentative identifications and total ion chromatograms from these analyses are summarized in Tables 5 to 12 and Figures 1 to 8. In general, EI ionization provides approximately equal ionization efficiency for all compound classes while NCI greatly favors ionization of electronegative compounds such as NO_2-PAH and OXY-PAH. Comparison of the EI and NCI GC/MS data may provide both fragmentation patterns and molecular ions for identification of unknown species.

As shown in Tables 5 through 8, most of the compounds identified from EI GC/MS analyses are non-active components, such as alkylbenzenes, aliphatic hydrocarbons, fatty acids, fatty acid esters and phthalates. Most of the polar PAH derivatives may be present at lower levels than their parent PAH, thus those compounds were not detected in EI GC/MS analyses. Since most of the compounds identified from EI GC/MS analyses were not biologically active, only day-zero samples were analyzed by this ionization mode.

Some PAH dicarboxylic acid anhydrides were tentatively identified from the NCI GC/MS analysis. To confirm the identifications of PAH dicarboxylic acid anhydrides, solutions of acenaphthylene and cyclopenta[c,d]pyrene which had been exposed to ultraviolet irradiation for 96 hr to form the respective dicarboxylic acid anhydrides were analyzed by EI and NCI GC/MS. The EI and

NCI mass spectra of naphthalene and pyrene dicarboxylic acid anhydrides are given in Figures 9 to 12. As shown in Figures 9 and 11, the characteristic neutral losses of CO_2 and CO are found in the EI spectra. As expected, only the molecular ion is detected in the NCI spectra. For the detection of these PAH dicarboxylic acid anhydrides, the NCI method is much more sensitive than the EI method. We can detect naphthalene and pyrene dicarboxylic acid anhydrides in the filter and XAD-2 samples only with the more sensitive NCI method, but not with the EI method. The relatively volatile naphthalene dicarboxylic acid anhydride was found mainly in the XAD-2 resin, and only small portions (<10 percent) of this compound were detected in the quartz fiber filters. The non-volatile pyrene dicarboxylic acid anhydride was detected only in the filter samples and not in the XAD-2 resin. The levels of these compounds from the day-30 samples were more than 1.5 times those of the day-0 samples. This finding clearly suggests that the acenaphthylene and cyclopenta[c,d]pyrene partially decompose to naphthalene and pyrene dicarboxylic acid anhydrides during storage.

There were a few other components including nitrogen containing compounds and oxygenated PAH that revealed increasing concentration trends during 30-day storage. The level of a tentatively identified hydroxynitropyrene isomer decreased to about 25 percent of its original value after storage. A few other unknown components indicated as MW153, MW268, and MW221 also revealed a similar decreasing concentration trend. We also found a few components such as MW198 and MW269 that were present only in the day-0 samples and not in the day-30 samples.

TRIPLE QUADRUPOLE MASS SPECTROMETRY ANALYSIS OF NO_2-PAH AND OXY-PAH STANDARDS AND SAMPLE EXTRACTS

The selected NO_2-PAH and OXY-PAH standards were analyzed by NCI MS/MS in the daughter spectral mode with either direct probe injection or GC splitless injection. The NCI, collision-activated dissociation (CAD) spectra of the standards are given in Appendix A. As shown in these spectra, the NO_2-PAH revealed characteristic CAD patterns, which are M^-, $(M-NO)^-$ and NO_2^-. For the dinitro PAH an additional fragment ion (M-2NO)- was also observed. The hydroxynitropyrene showed the same pattern of

fragmentation ions as the NO_2-PAH, as well as $(M-NO-OH)^-$. Thus, with this CAD technique, the selected ion fragmentation process for NO_2-PAH and OH-NO_2-PAH can provide more selectivity and discrimination over the conventional GC/MS method. However, the estimated detection sensitivity of NCI MS/MS, in general, is lower than the conventional NCI GC/MS technique. The detection sensitivity can be improved by performing the MS/MS at optimum instrumental sensitivity. This would entail initiating the experiments with cleaned ion source lenses and analyzer rods. Operating conditions for the CAD processing, such as collision energy, gas pressure, and instrumental tuning, can also be optimized to improve the detection sensitivity. More investigations need to be carried out in order to obtain a true comparison of detection limits for NO_2-PAH and OH-NO_2-PAH from those two techniques with NCI GC/MS/MS and NCI GC/MS.

In order to determine whether some nitrogen containing compounds tentatively identified from NCI GC/MS methods (Table 9 to 12) contained NO_2 functional groups, the sample extracts were reanalyzed by NCI GC/MS/MS. None of these unknown components were confirmed to contain NO_2 functional groups when Q3 was operated at full mass scan mode. Since the absolute detection sensitivity of GC/MS/MS is less than that of GC/MS, it is possible the CAD fragmentation ions were below detection limits.

The extracts were reanalyzed with the Q3 operated in a MID mode monitoring the specific daughter ions. The monitored ions were selected based on the assumption that these unknown compounds contained NO_2 groups. There are few compounds confirmed to contain NO_2 functional groups from these analyses. The results are summarized in Table 13. It was noted that the CAD spectrum of a tentatively identified hydroxynitropyrene isomer from NCI GC/MS analysis was not detected even with the Q3 operated at the MID mode.

There were no characteristic fragmentation patterns for OXY-PAH standards observed in the NCI MS/MS analysis. In most cases, only the molecular ions were present in the CAD spectra. This finding indicates that the OXY-PAH are too stable to fragment in the CAD process. We tried to increase the collision energy to the limit of the TSQ instrument (30 volts) and still were unable to obtain the expected loss of $(M-CO)^{-\cdot}$. Thus, it

appears that NCI GC/MS/MS technique is not applicable to the determination of OXY-PAH.

Because the NCI, CAD process cannot provide any characteristic fragmentation patterns of OXY-PAH, these standards were reanalyzed by PCI MS/MS to determine the CAD fragmentation patterns. The PCI, CAD spectra of OXY-PAH are given in Appendix B. Unlike the NCI mode, there were specific CO losses from all OXY-PAH including polynuclear aromatic aldehydes, polynuclear aromatic ketones, and polynuclear aromatic acid anhydrides. The results suggested that PCI MS/MS can be used to determine OXY-PAH, however more studies are needed to optimize the detection sensitivity.

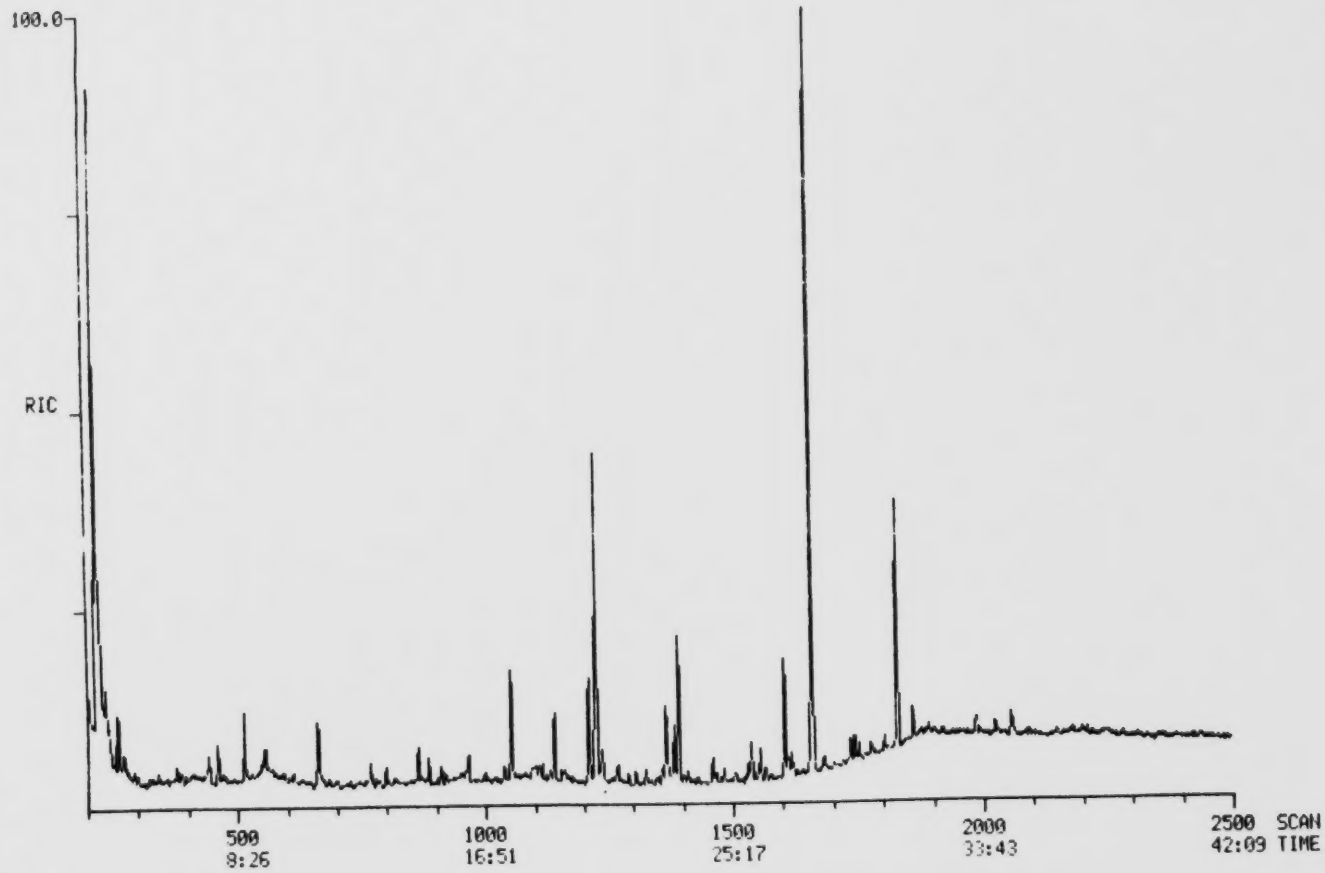

Figure 1. The EI GC/MS total ion current chromatogram of the day-0 filter sample

TABLE 5. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE FILTER SAMPLE FROM THE EI GC/MS ANALYSIS

Scan No.(a)	Tentative Identification
220	Aliphatic alcohol
262	Unknown
443	Benzoic acid
461	Unknown
471	Aliphatic hydrocarbon
515	Unknown
665	Unknown
768	Phthalate
799	Silicone
865	Fatty acid
967	Silicone
1000	Aliphatic hydrocarbon
1054	Fatty acid
1142	Fatty acid
1212	Aliphatic hydrocarbon
1228	Fatty acid
1239	Phthalate
1270	Aliphatic hydrocarbon
1327	Aliphatic hydrocarbon
1368	Aliphatic hydrocarbon
1384	Fatty acid
1393	Fatty acid ester
1460	Fatty acid ester
1538	Phthalate
1556	Fatty acid ester
1605	9-phenylanthracene (internal standard)

TABLE 5. (continued)

Scan No.(a)	Tentative Identification
1619	Aliphatic hydrocarbon
1661	Phthalate
1745	Aliphatic hydrocarbon
1804	Aliphatic hydrocarbon
1829	Aliphatic hydrocarbon
1861	Aliphatic hydrocarbon
1986	Aliphatic hydrocarbon

(a) The scan numbers are from the analysis of the day-0 filter sample.

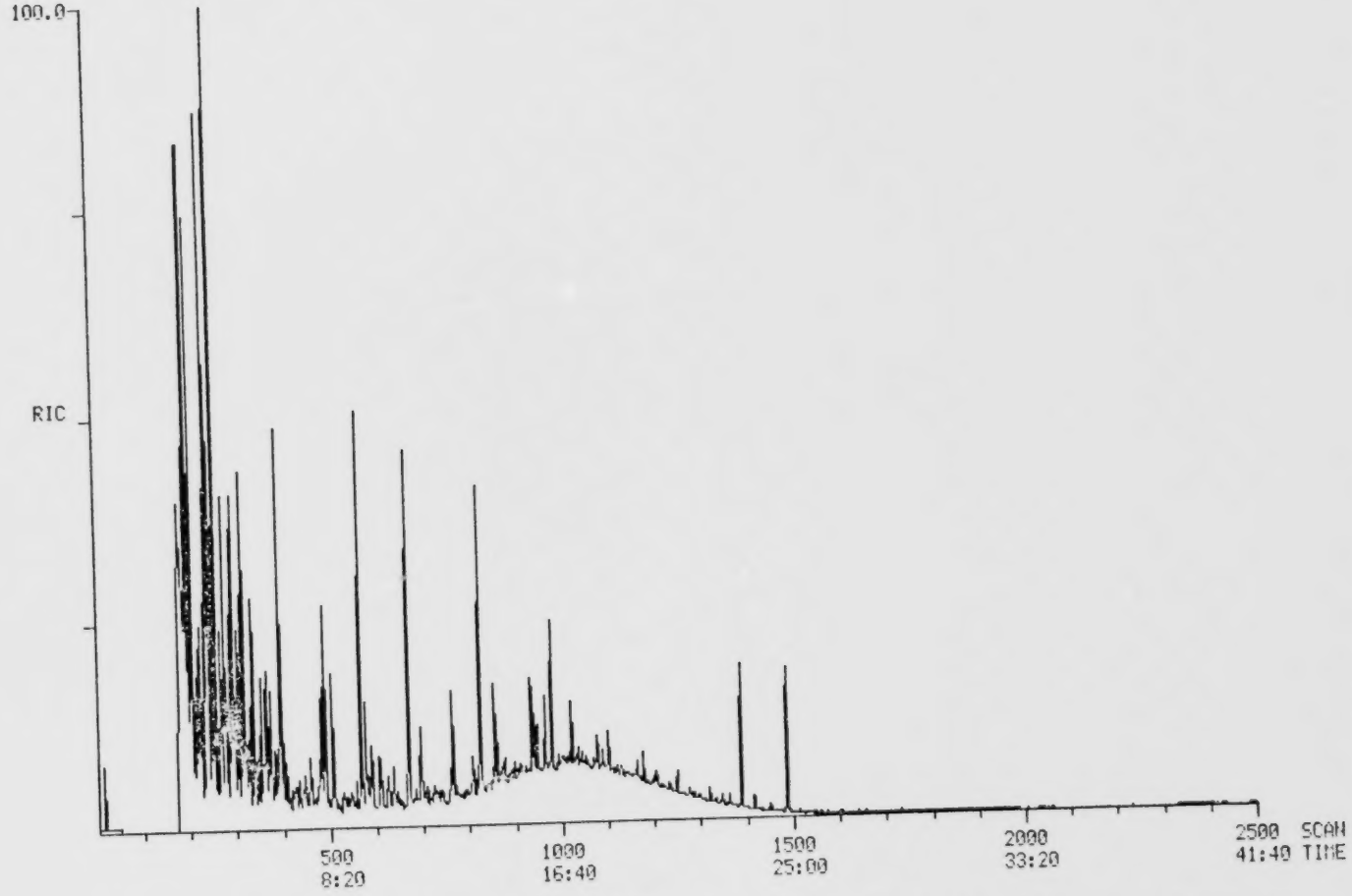

Figure 2. The EI GC/MS total ion current chromatogram of the hexane/benzene fraction of the day-0 XAD-2 sample

TABLE 6. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE HEXANE/BENZENE FRACTION OF THE XAD-2 SAMPLE FROM THE EI GC/MS ANALYSIS

Scan No.(a)	Tentative Identification
209	MW 106, C_2, benzene
241	MW 120, C_3, benzene
250	MW 120, C_3, benzene
259	MW 120, C_3, benzene
270	MW 146, dichlorobenzene
276	MW 120, C_3, benzene
296	MW 134, C_4, benzene
315	MW 134, C_4, benzene
331	MW 134, C_4, benzene
338	MW 134, C_4, benzene
366	Mixture, MW 134 C_4, benzene and MW 132, alkyl benzene
374	MW 134, C_4, benzene
383	MW 148, C_5, benzene
396	MW 128, naphthalene
486	Aliphatic hydrocarbon
492	MW 142, C_1, naphthalene
508	MW 142, C_1, naphthalene
571	MW 154, 1,1-biphenyl
579	Aliphatic hydrocarbon
607	MW 156, C_2, naphthalene
672	Silicone
696	Fatty acid ester
766	Aliphatic hydrocarbon

TABLE 6. (continued)

Scan No.(a)	Tentative Identification
828	Silicone
855	Aliphatic hydrocarbon
937	MW 178, Phenanthrene
981	Aliphatic hydrocarbon
1024	Aliphatic hydrocarbon
1390	Phthalate
1417	9-phenylanthracene (internal standard)
1489	Phthalate

(a) The scan numbers are from the analysis of the day-0 filter sample.

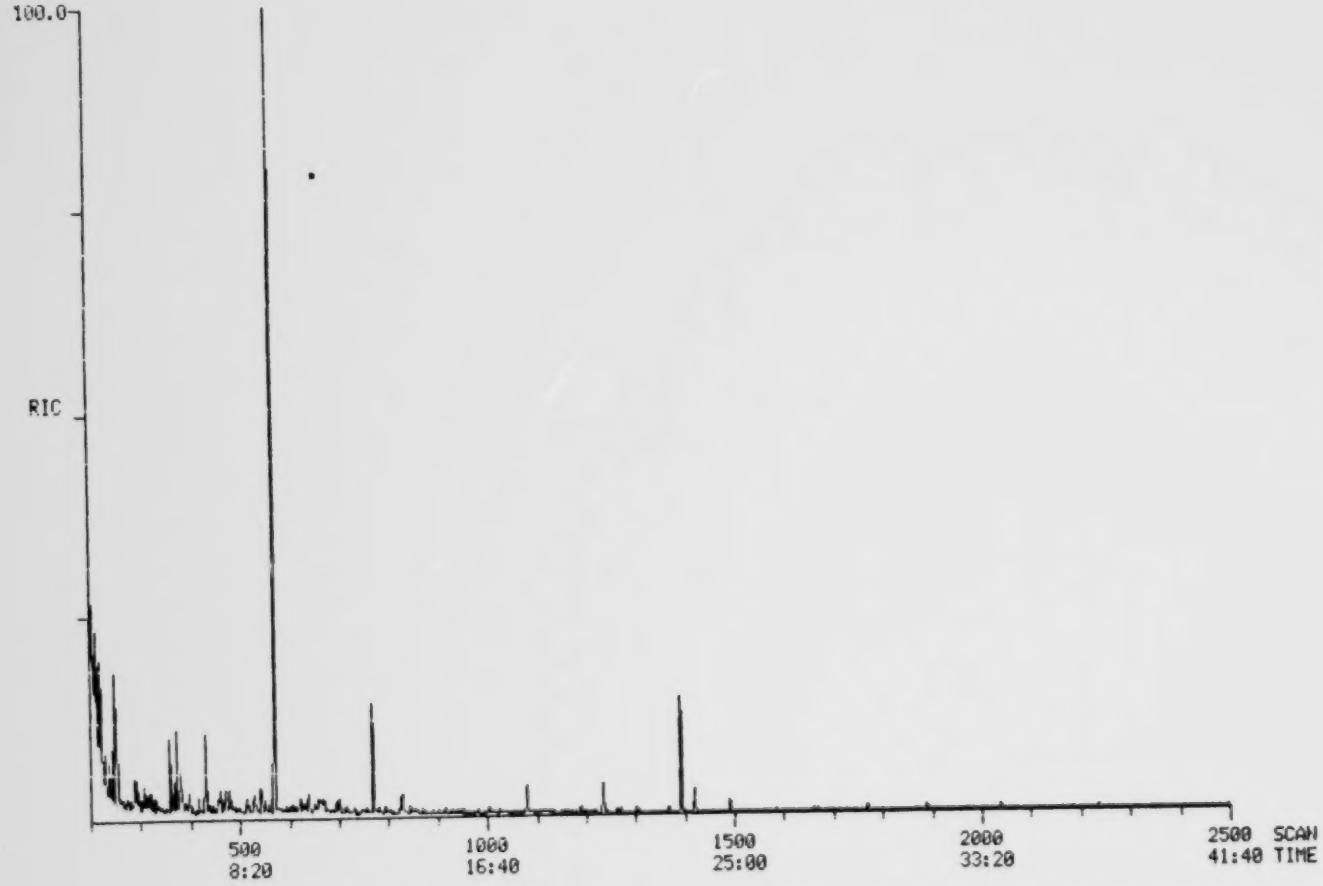

Figure 3. The EI GC/MS total ion current chromatogram of the dichloromethane fraction of the day-0 XAD-2 sample

TABLE 7. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE DICHLOROMETHANE FRACTION OF THE XAD-2 SAMPLES FROM THE EI GC/MS ANLAYSIS

Scan No.(a)	Tentative Identification
251	Phenol
360	MW 152, C_3, bicyclo(3,1,1)heptanone
374	MW 152, isomer of #360
380	C_2, phenol
432	MW 135, benzothiazole
572	MW 154, 1,1-biphenyl
769	Phthalate
1081	Phthalate
1235	Fatty acid ester
1393	Fatty acid ester
1421	9-phenylanthracene (internal standard)
1492	Phthalate

(a) The scan numbers are from the analysis of the day-0 CH_2Cl_2 fraction of the XAD-2 samples.

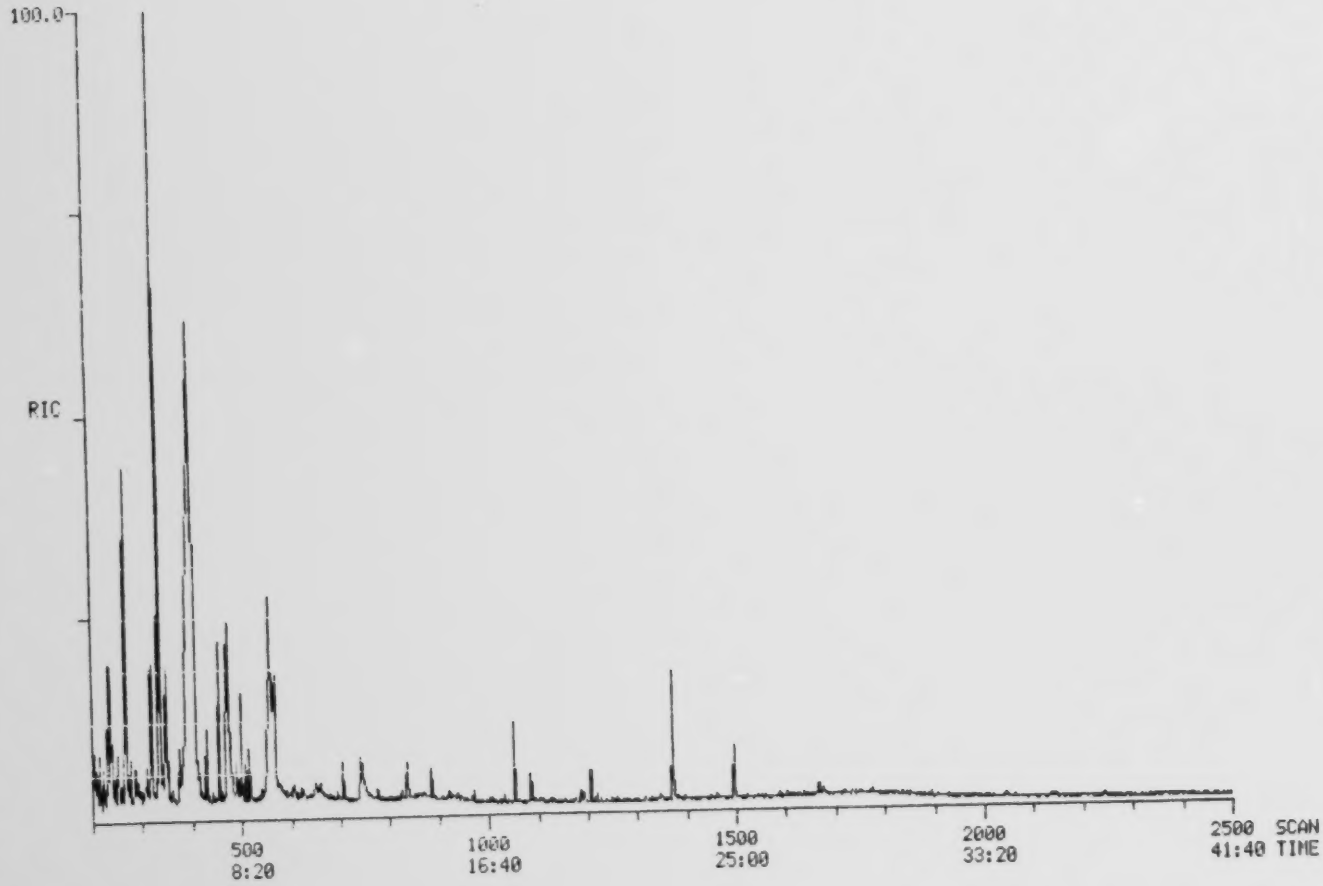

Figure 4. The EI GC/MS total ion current chromatogram of the methanol fraction of the day-0 XAD-2 sample

TABLE 8. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE METHANOL FRACTION OF THE XAD-2 SAMPLES FROM THE EI GC/MS ANALYSIS

Scan No.(a)	Tentative Identification
233	Fatty acid
236	Fatty acid ester
271	Fatty acid
321	Fatty acid
338	Benzoic acid methyl ester
351	Fatty acid
408	Benzoic acid
431	Fatty acid ester
476	Fatty acid
500	C_2, benzoic acid methyl ester
508	MW 157, dibutylformamide
514	C_2, benzoic acid
560	C_2, benzoic acid
569	C_2, benzoic acid
706	Fatty acid ester
886	Fatty acid ester
1053	Fatty acid ester
1087	Phthalate
1207	Fatty acid ester
1373	Phthalate
1497	Phthalate

(a) The scan numbers are from the analysis of the day-0 MEOH fraction of the XAD-2 sample.

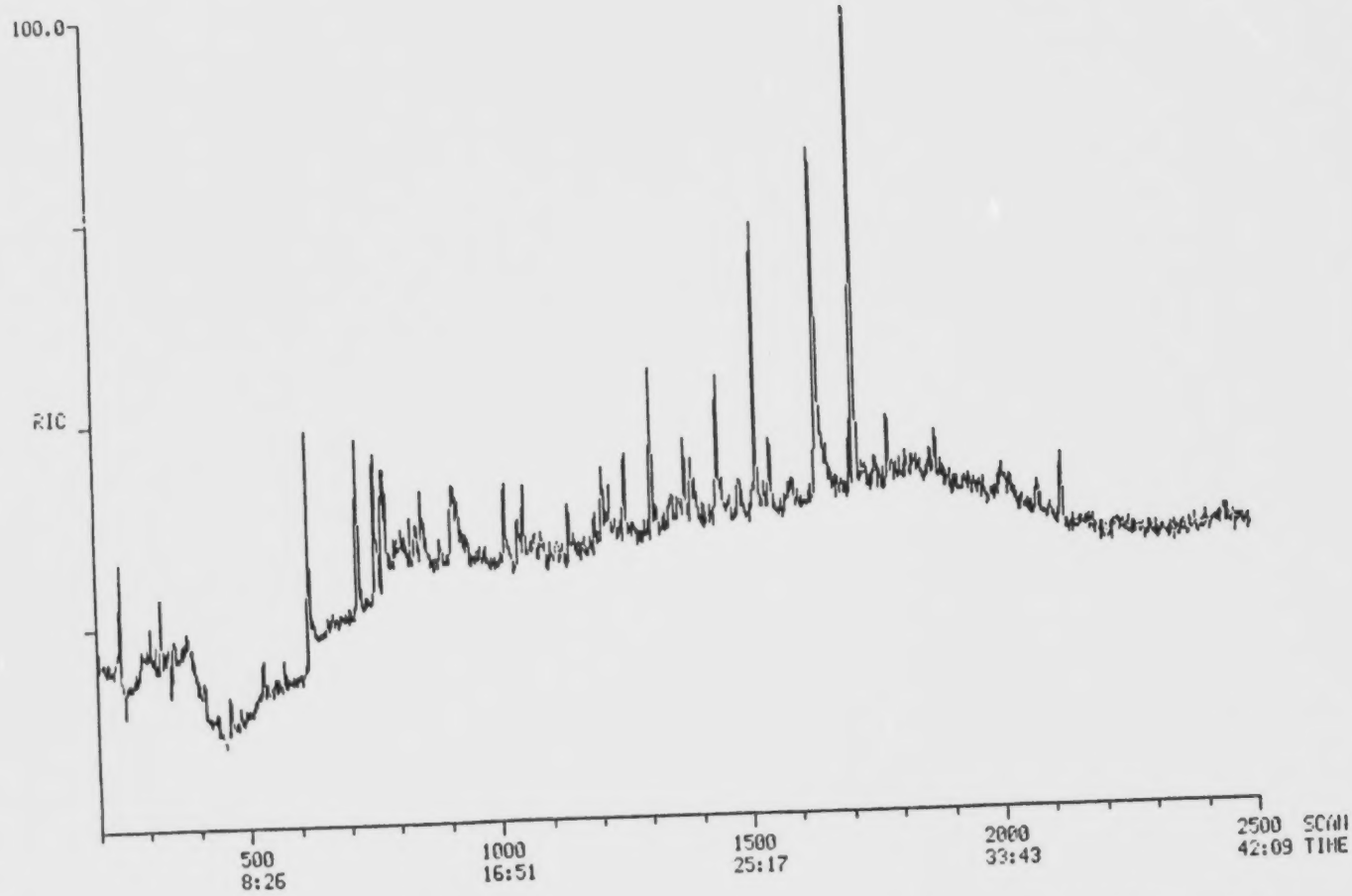

Figure 5. The NCI GC/MS total ion current chromatogram of the day-0 filter sample

TABLE 9. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE FILTER SAMPLES FROM THE NCI GC/MS ANALYSIS

Scan No. (a)	Tentative Identification	Ratio Day-0 Value/Day-30 Value
249	MW 112, unknown	2
467	MW 125, N- containing compound	1
486	MW 182, unknown	0.5
575	MW 111, N- containing compound	NA(b)
625	Phthalate	1
724	MW 162, unknown	2
758	MW 162, isomer of #724	2
771	MW 146, unknown	SAT(c)
779	MW 218, unknown	SAT(c)
812	MW 197, N- containing compound	0.6
828	MW 169, N- containing compound	1
841	MW 138, unknown	1
851	Mixture, MW 176 and MW 198	1
888	MW 176, unknown	1
925	MW 176, isomer of #888	1
1018	MW 120, unknown	0.2
1043	MW 191, N- containing compound	0.5
1055	MW 180, fluorenone	0.7
1132	Mixture, MW 253 and MW 194 methyl-fluorenone or OH-anthracene/phenanthrene isomer	0.7
1145	MW 198, unknown	0.7
1197	MW 181, N- containing compound	0.5
1199	MW 229, N- containing compound	NA(b)
1258	MW 208, C_2-alkyl fluorenone or anthracene/phenanthrenedione isomer	0.6

TABLE 9 (Continued)

Scan No. (a)	Tentative Identification	Ratio, Day-0 Value/Day-30 Value
1310	MW 223, NO_2-anthracene/phenanthrene isomer	0.8
1311	MW 198, naphthalene-1,8-dicarboxylic acid anhydride	0.8
1322	Mixture, MW 188 and MW 204	0.8
1352	MW 198, unknown	NA(b)
1365	MW 222, methyl anthracene/phenanthrene dione isomer	1
1377	Silicone	1
1392	Mixture, MW 194 and MW 212	1
1394	MW 223, isomer of # 1310	0.9
1400	MW 212, unknown	1
1444	Mixture, MW 212 and MW 342	2
1522	Mixture, MW 211 N- containing compound and MW 226	0.6
1550	MW 230, possible benzofluorenone isomer	0.7
1573	MW 230, isomer of #1550	0.8
1591	MW 230, isomer of # 1550	0.8
1642	Phthalate	1
1649	MW 230, pyrenecarboxaldehyde	0.9
1661	MW 277, possible OH- NO_2- C_2 alkyl fluoranthene isomer	0.8
1678	MW 247, 2/3-NO_2 -fluoranthene	0.9
1708	MW 258, benz[a]anthracene-7,12-dione	0.9
1718	MW 256, D_9-1-NO_2-pyrene (internal standard)	1
1721	MW 247, 1-NO_2-pyrene	0.7
1783	MW 263, possible OH-NO_2-fluoranthene/pyrene isomer	4
1785	MW 248, dicarboxylic acid anhydride from PAH with MW 202	0.7
2078	MW 272, pyrene-3,4-dicarboxylic acid anhydride	0.6

TABLE 9. (Continued)

Scan No. (a)	Tentative Identification	Ratio, Day-0 Value/Day-30 Value
2102	MW 278, possible dibenzo[a,h] anthracene isomer	0.9
2125	MW 276, possible benzo[g,h,i]perylene isomer	1

(a) The scan numbers are from the analysis of the day-0 filter sample.

(b) This compound was not found in the day-30 filter sample.

(c) The saturated peaks were found in both day-0 and day-30 filter samples.

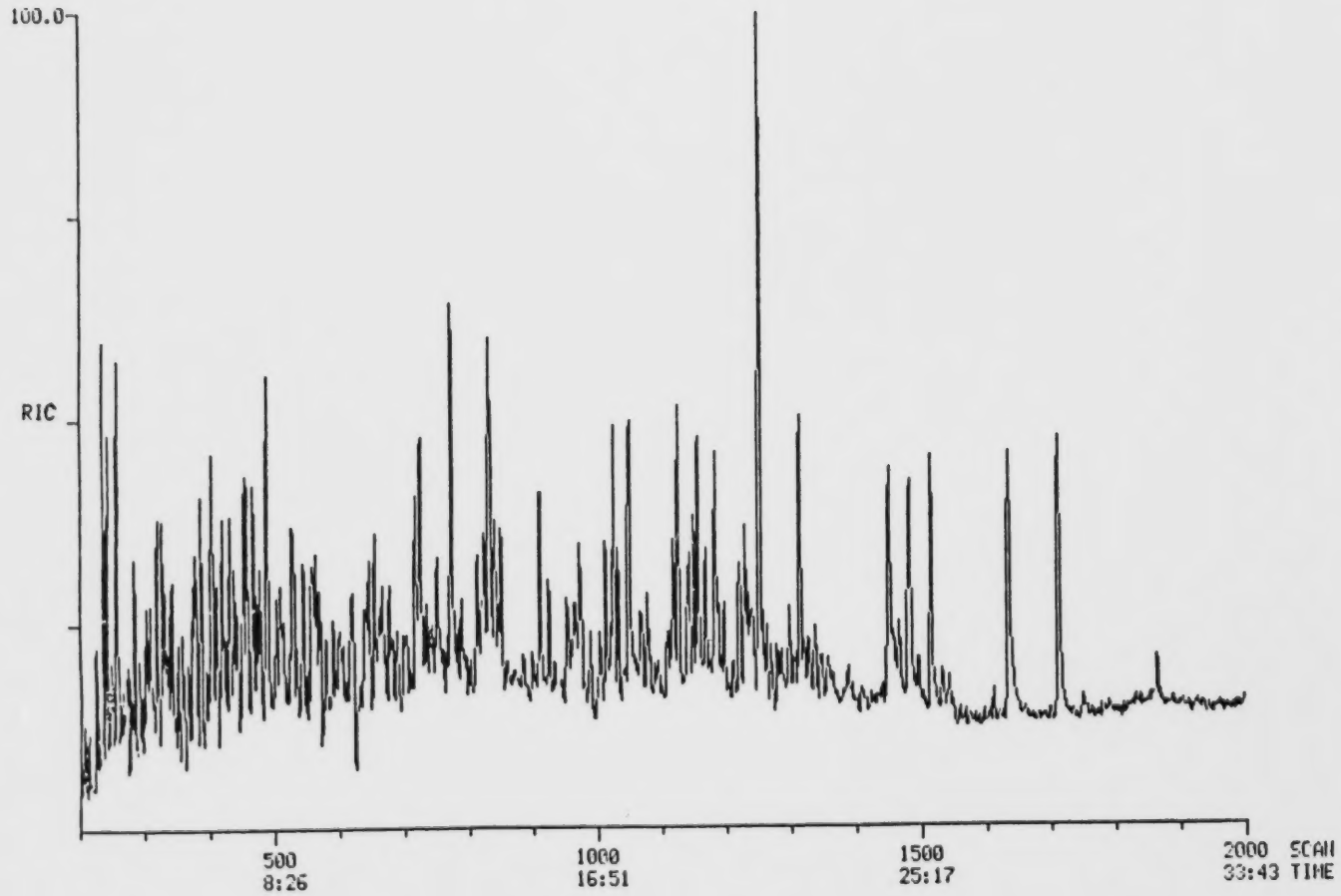

Figure 6. The NCI GC/MS total ion current chromatogram of the hexane/benzene fraction of the day-0 XAD-2 sample

TABLE 10. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE HEXANE/BENZENE FRACTIONS OF THE XAD-2 SAMPLES FROM THE NCI GC/MS ANALYSIS

Scan No.(a)	Tentative Identification	Ratio, Day-0 Value/Day-30 Value
387	MW 140, unknown	SAT(b)
545	MW 153, possible OH-NO_2-methylbenzene	1
691	MW 153, isomer of #545	0.7
726	MW 159, N- containing compound	SAT(b)
774	MW 220, unknown	SAT(b)
833	MW 173, NO_2-naphthalene	SAT(b)
912	MW 236, unknown	SAT(b)
925	MW 173, isomer of #833	1
965	MW 173, isomer of #833	1
1052	MW 180, fluorenone	SAT(b)
1119	Possible Cl-containing compound	1
1127	MW 253, possible OH-NO_2-methyl-anthracene/phenanthrene isomer	1
1188	MW 208, C_2-alkylfluorenone or anthracene/phenanthrenedione	SAT(b)
1198	MW 208, isomer of #1188	SAT(b)
1251	MW 208, isomer of #1188	1
1270	MW 208, isomer of #1188	1
1280	MW 208, isomer of #1188	1
1315	MW 205, N- containing compound	SAT(b)
1359	MW 222, possible methylanthracene/phenanthrenedione isomer	1
1389	MW 223, NO_2-anthracene/phenanthrene isomer	1
1449	MW 223, isomer of #1389	1
1455	MW 213, N- containing compound	0.7
1476	MW 223, isomer of #1389	1
1517	MW 221, N- containing compound	SAT(b)

TABLE 10. (Continued)

Scan No.[a]	Tentative Identification	Ratio Day-0 Value/Day-30 Value
1533	MW 269, N- containing compound	NA[c]
1544	MW 230, possible benzofluorenone isomer	1
1569	MW 230, isomer of #1544	1
1636	Phthalate	1
1713	D_9-1-NO_2-pyrene (internal standard)	1

(a) The scan numbers are from the analysis of the day-0 hexane/benzene fraction of the XAD-2 sample.

(b) The saturated peaks were found in both day-0 and day-30 samples.

(c) This compound was not found in the day-30 sample.

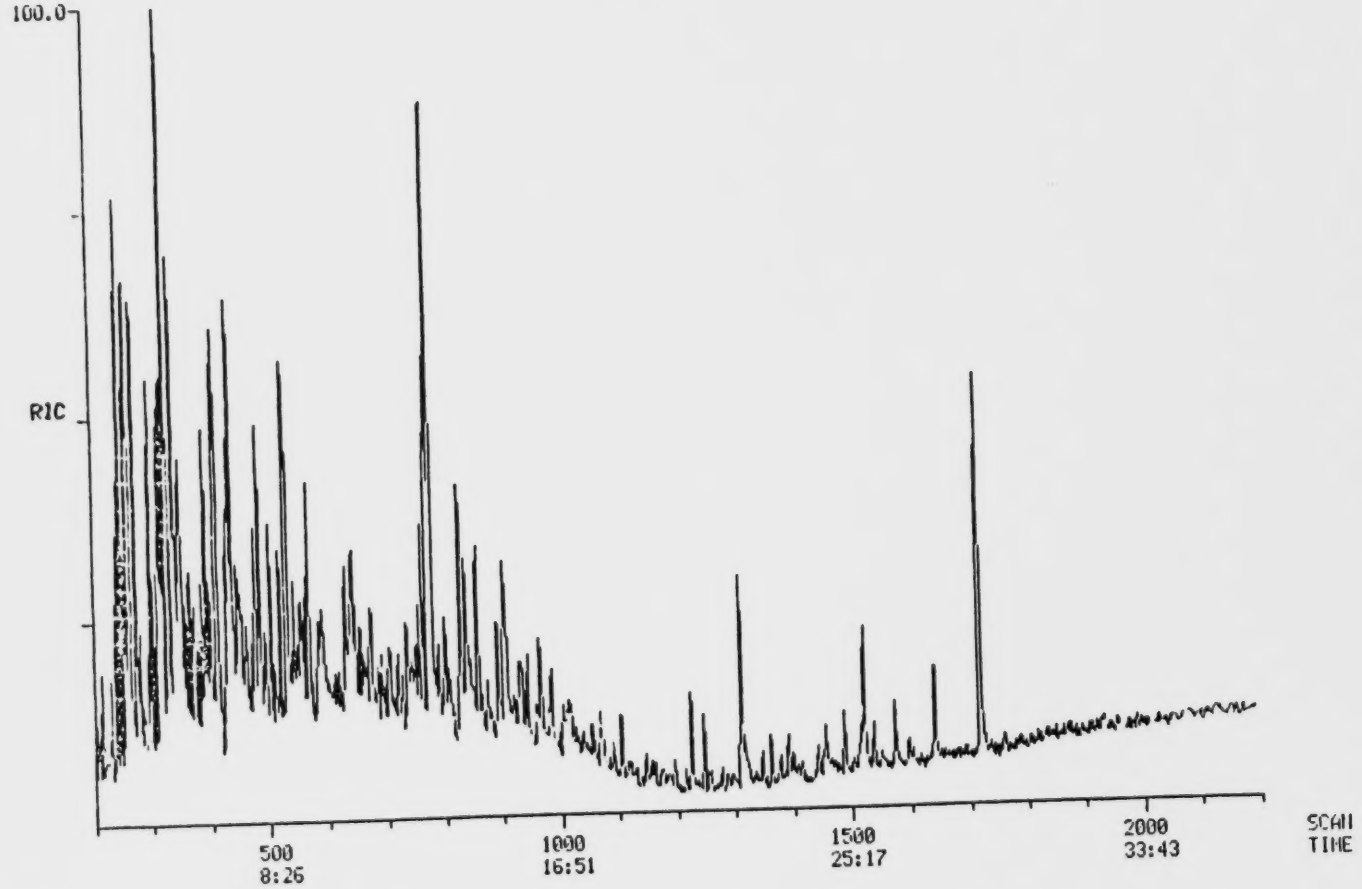

Figure 7. The NCI GC/MS total ion current chromatogram of the dichloromethane fraction of the day-0 XAD-2 sample

TABLE 11. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE DICHLOROMETHANE FRACTIONS OF THE XAD-2 SAMPLES FROM THE NCI GC/MS ANALYSIS

Scan No.(a)	Tentative Identification	Ratio Day-0 Value/Day-30 Value
248	MW 112, unknown	SAT(b)
261	MW 112, isomer, #248	SAT(b)
273	MW 109, N- containing compound	SAT(b)
326	MW 126, unknown	SAT(b)
339	MW 126, isomer of #326	SAT(b)
393	MW 140, unknown	SAT(b)
410	MW 117, N- containing compound	SAT(b)
438	MW 152, unknown	SAT(b)
530	MW 130, unknown	SAT(b)
562	MW 139, possible OH-NO_2-benzene	0.5
570	MW 153, N- containing compound	4
657	MW 139, isomer of #562	0.7
756	MW 169, N- containing compound	SAT(b)
778	Mixture, MW 146 & MW 218	SAT(b)
828	MW 169, isomer of #756	SAT(b)
903	MW 193, N- containing compound	SAT(b)
918	MW 173, NO_2-naphthalene	1
1014	MW 268, unknown	3
1054	MW 180, fluorenone	0.7
1090	MW 194, unknown	0.6
1256	MW 208, possible C_2-alkylfluorenone or anthracene/phenanthrenedione	1.1
1310	MW 198, naphthalene-1,8-dicarboxylic acid anhydride	0.6

TABLE 11. (Continued)

Scan No.(a)	Tentative Identification	Ratio Day-0 Value/Day-30 Value
1347	MW 222, possible methylanthracene/ phenanthrenedione	1
1521	MW 221, N- containing compound	0.7
1538	MW 269, N- containing compound	NA(c)
1642	Phthalate	1
1719	D_9-1-NO_2-pyrene (internal standard)	1

(a) The scan numbers are from the analysis of the day-0 CH_2Cl_2 fraction of the XAD-2 samples.

(b) The saturated peaks were found in both day-0 and day-30 samples.

(c) This compound was not found in the day-30 sample.

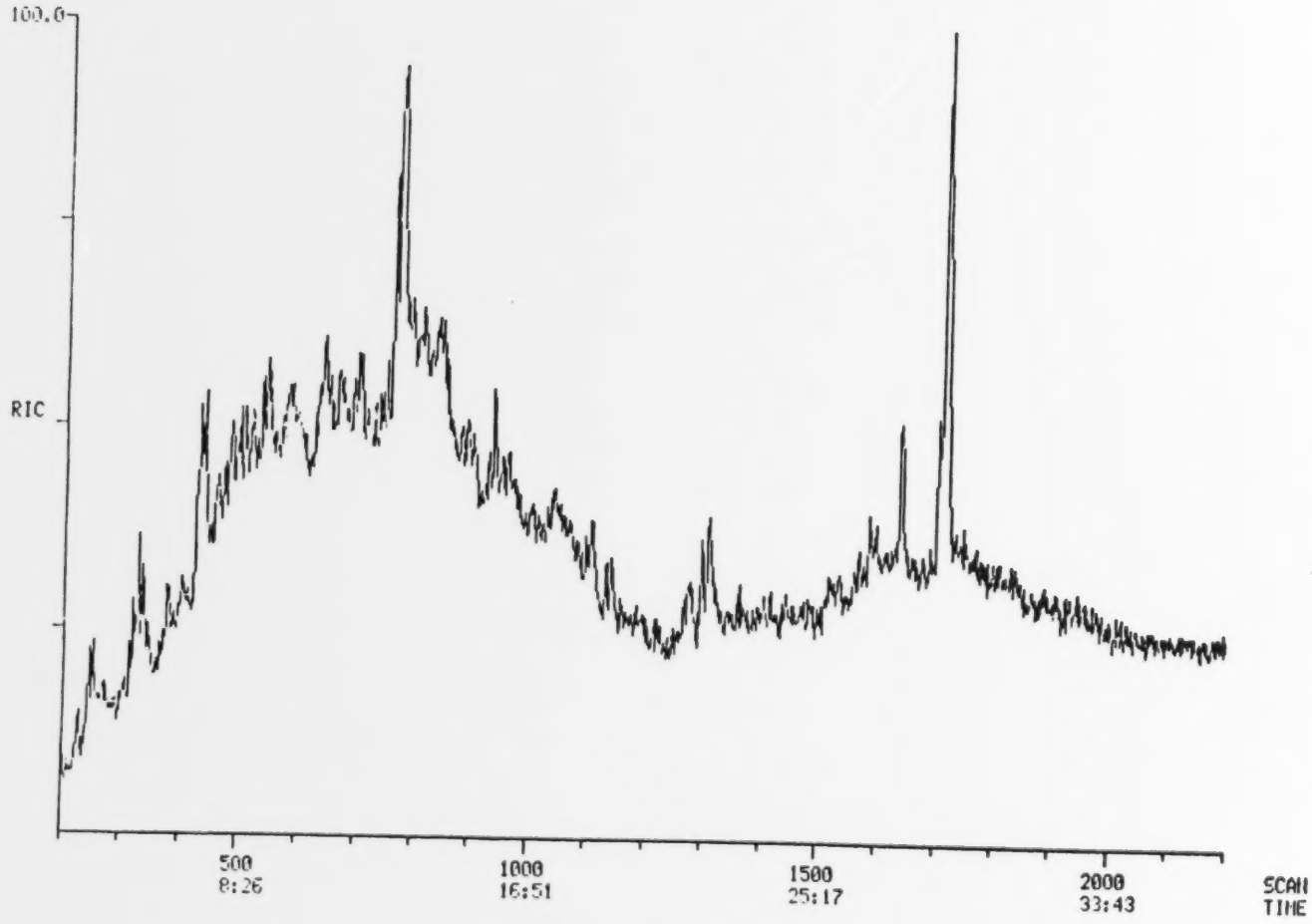

Figure 8. The NCI GC/MS total ion current chromatogram of the methanol fraction of the day-0 XAD-2 sample

TABLE 12. TENTATIVE IDENTIFICATION OF COMPOUNDS IN THE METHANOL FRACTION OF THE XAD-2 SAMPLES FROM THE NCI GC/MS ANALYSIS

Scan No. (a)	Tentative Identification	Ratio, Day-0 Value/Day-30 Value
227	MW 113, N- containing compound	2
239	MW 112, unknown	4
316	MW 139, possible OH-NO_2-benzene	0.6
382	MW 125, N- containing compound	1
549	MW 169, N- containing compound	2
772	Mixture, MW 146, and MW 218	SAT(b)
956	MW 203, N- containing compound	0.7
958	MW 116, unknown	10
962	MW 203, N- containing compound	2
963	MW 116, unknown	7
1513	MW 221, N- containing compound	40
1640	Phthalate	1
1709	D_9-1-NO_2-pyrene (internal standard)	1

(a) The scan numbers are from the analysis of the day-0 MEOH fraction of the XAD-2 sample.

(b) The saturated peaks were found in both the day-0 and the day-30 MEOH fractions.

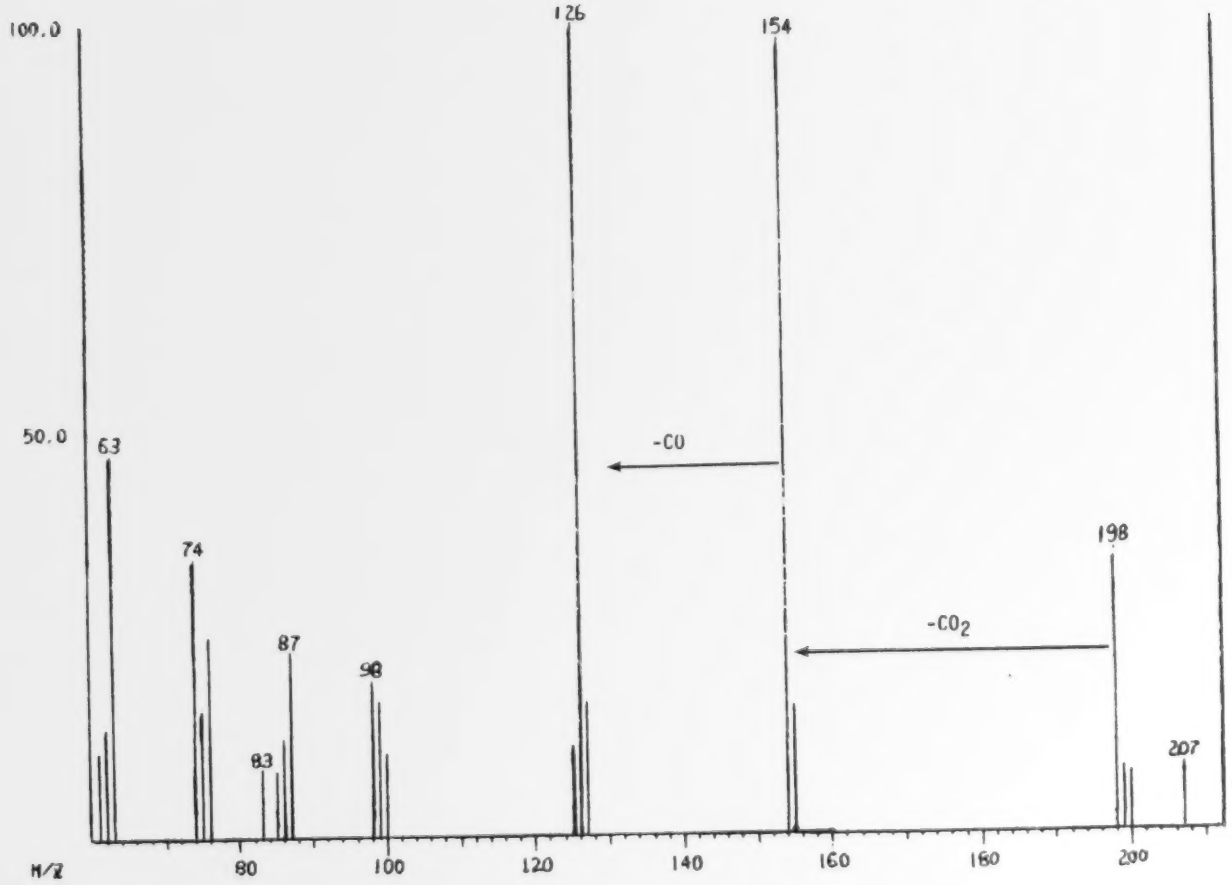

Figure 9. The EI spectrum of naphthalene-1,8-dicarboxylic acid anhydride, m/z 198

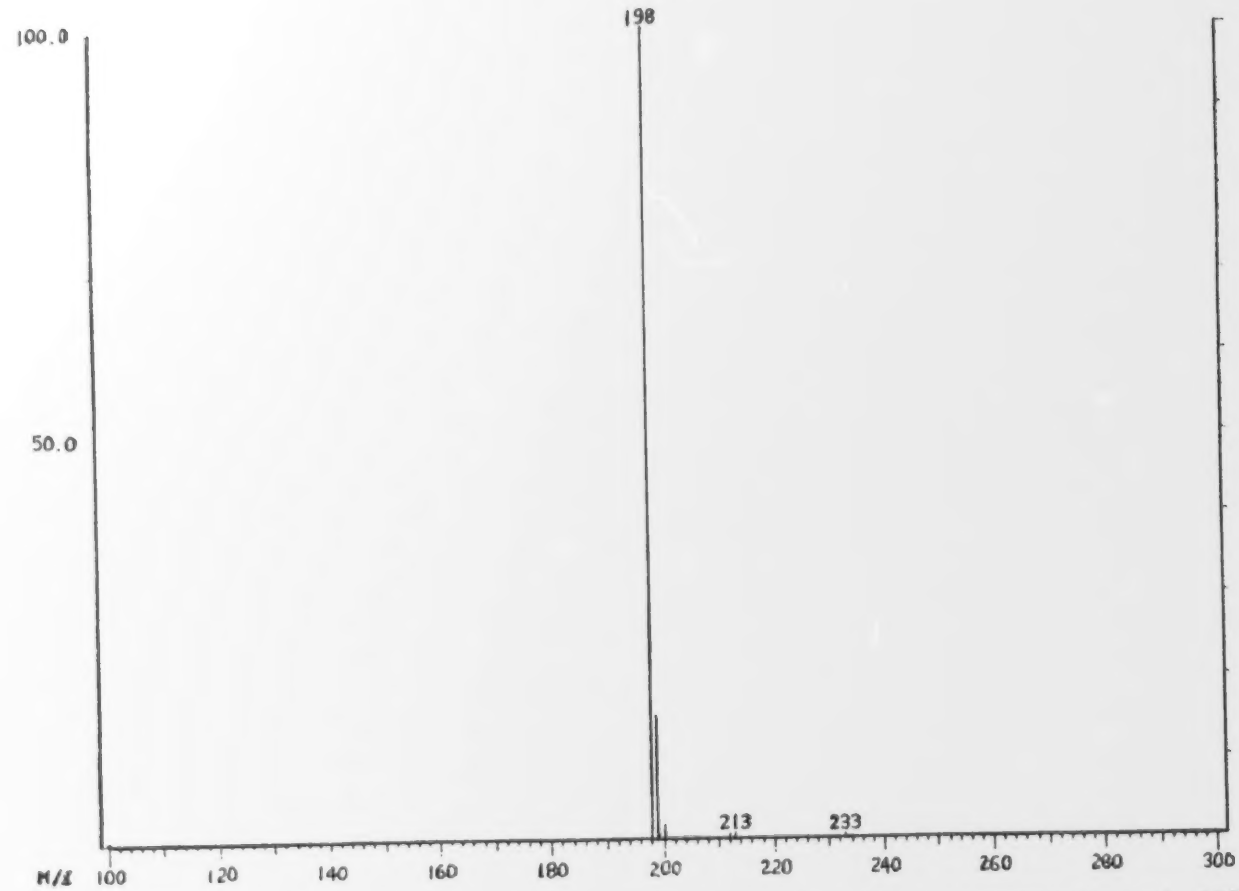

Figure 10. The NCI spectrum of naphthalene-1,8-dicarboxylic acid anhydride, m/z 198

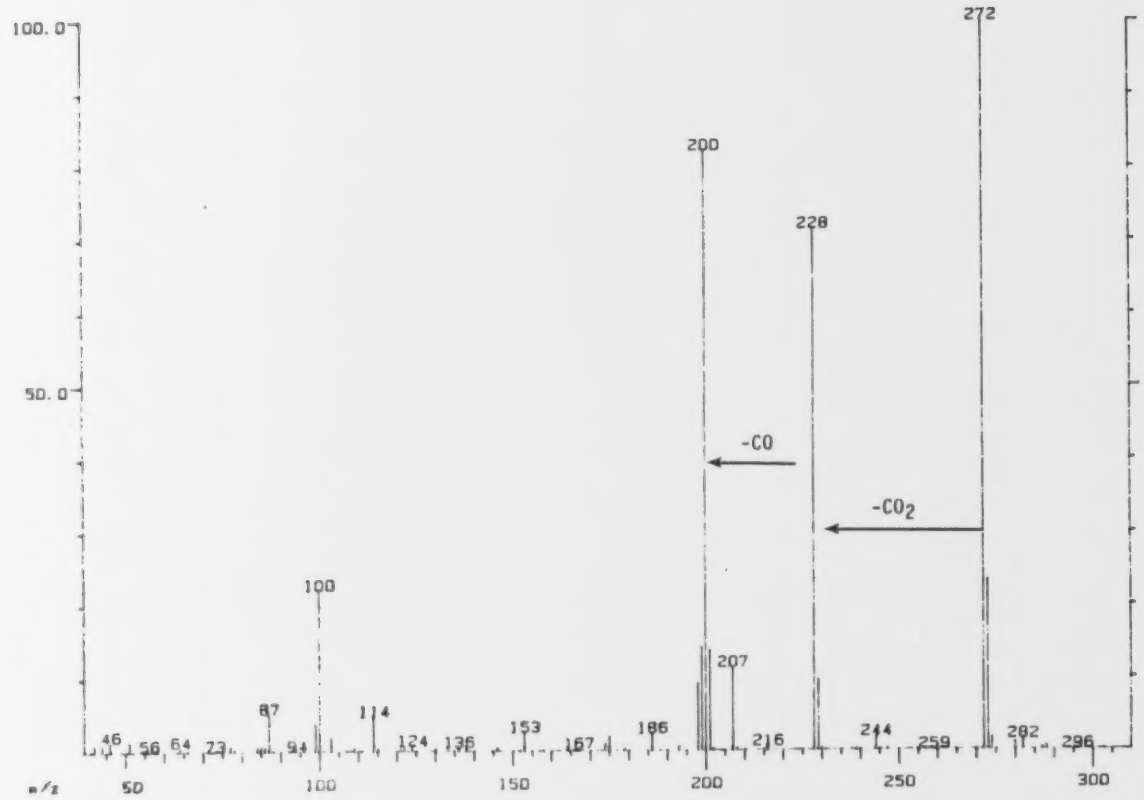

Figure 11. The EI spectrum of pyrene-3,4-dicarboxylic acid anhydride, m/z 272

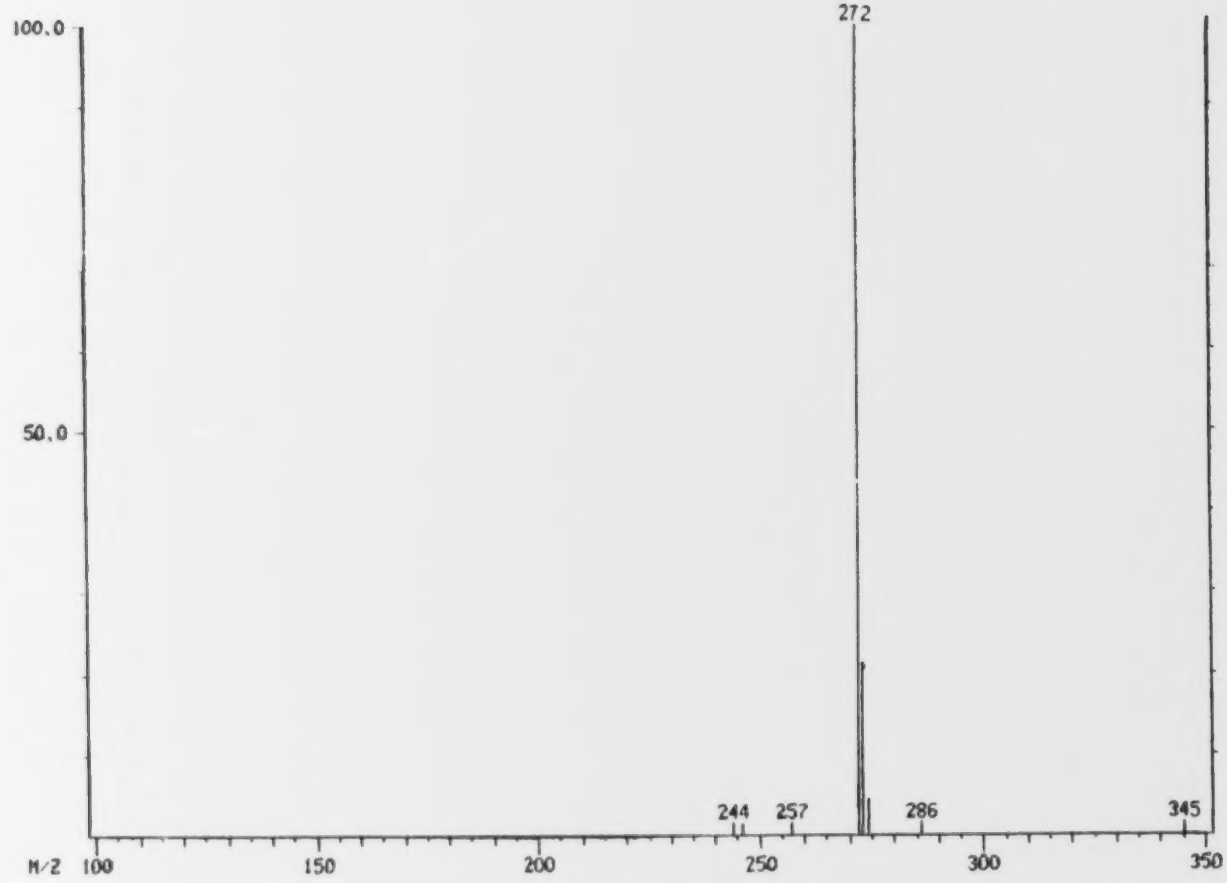

Figure 12. The NCI spectrum of pyrene-3,4-dicarboxylic acid anhydride, m/z 272

TABLE 13. COMPOUNDS CONTAINING NITRO FUNCTIONAL GROUPS BY NCI GC/MS/MS

Molecular ion, m/z	Sample type
181	Filter total extract
205	XAD-2, hexane/benzene fraction
117	XAD-2, dichloromethane fraction
139	XAD-2, dichloromethane fraction
153	XAD-2, dichloromethane fraction
169	XAD-2, dichloromethane fraction
193	XAD-2, dichloromethane fraction

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APPENDIX A

THE NCI DAUGHTER SPECTRA OF NO_2-PAH AND OXYGENATED PAH

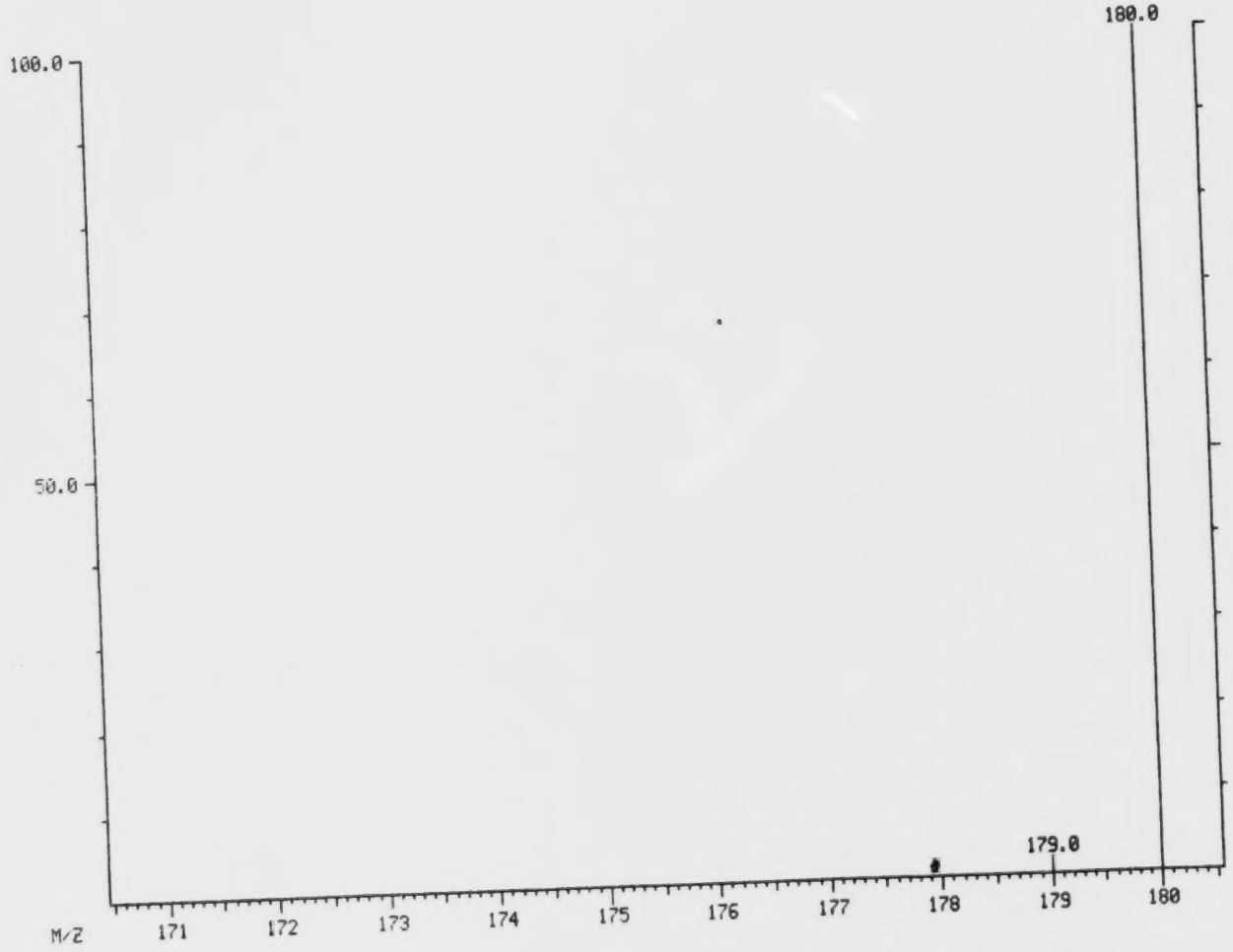

Figure A-1. The NCI daughter spectrum of fluorenone, m/z 180

Figure A-2. The NCI daughter spectrum of pyrenecarboxaldehyde, m/z 230

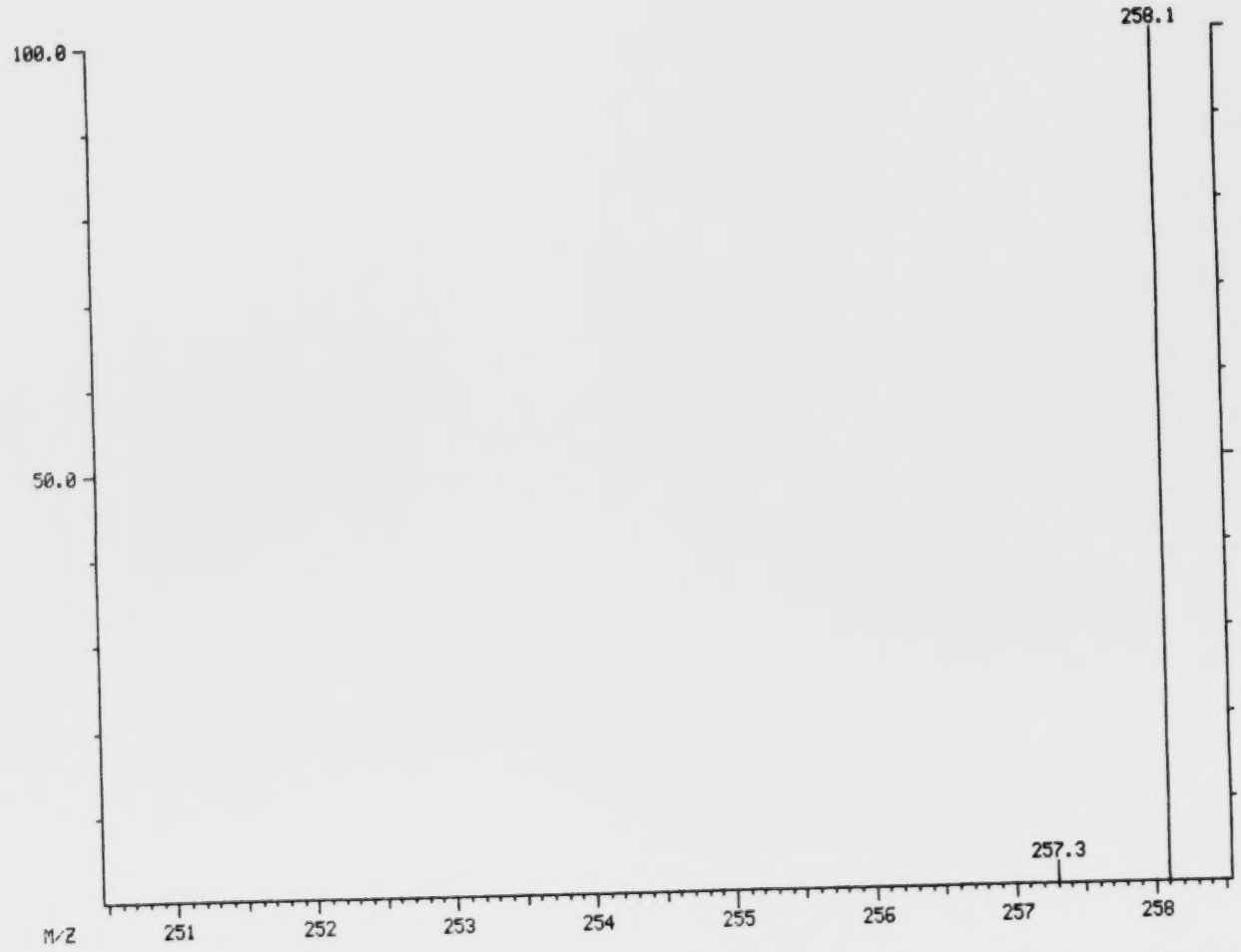

Figure A-3. The NCI daughter spectrum of benz[a]anthracene-7,12-dione, m/z 258

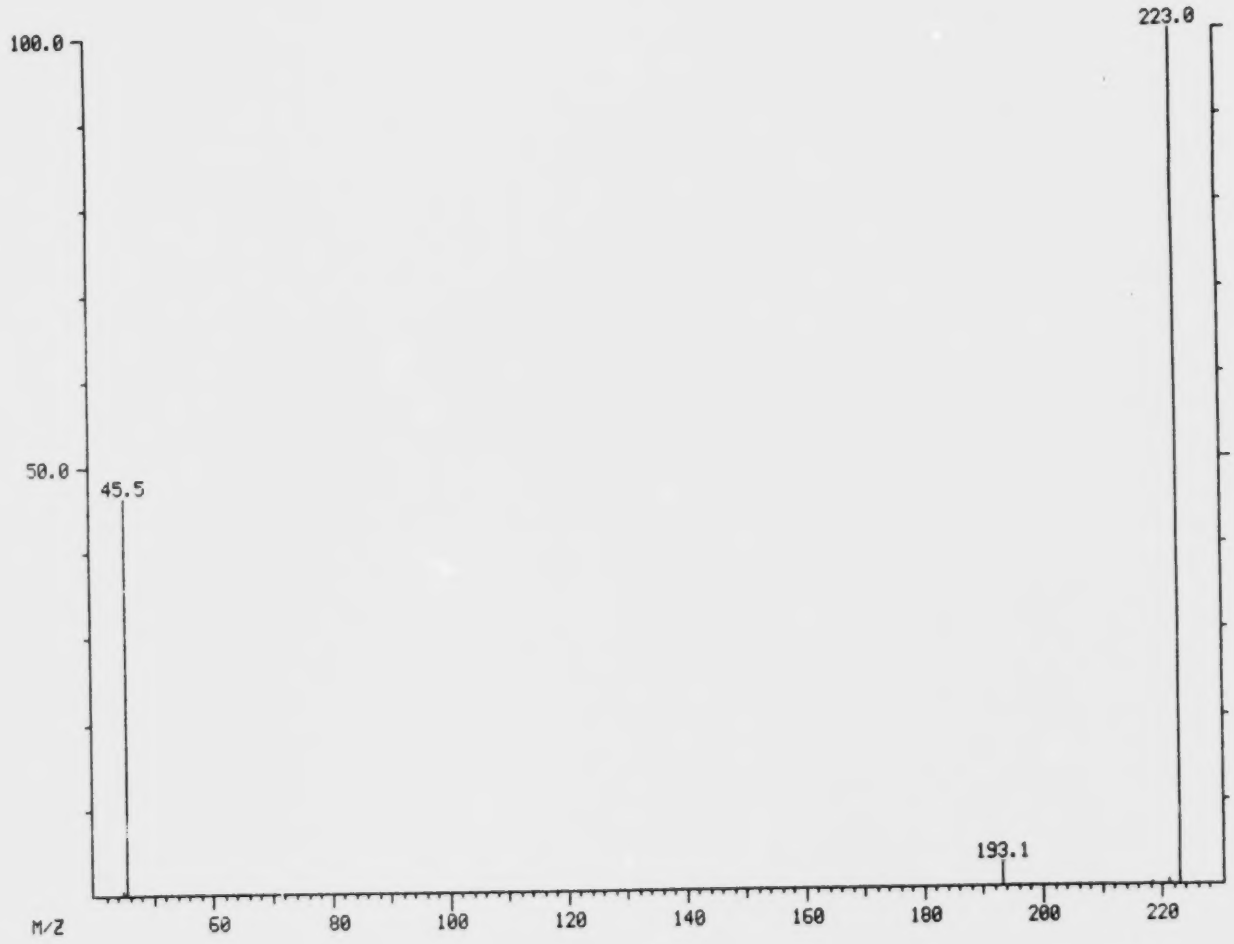

Figure A-4. The NCI daughter spectrum of 9-nitrophenanthrene, m/z 223

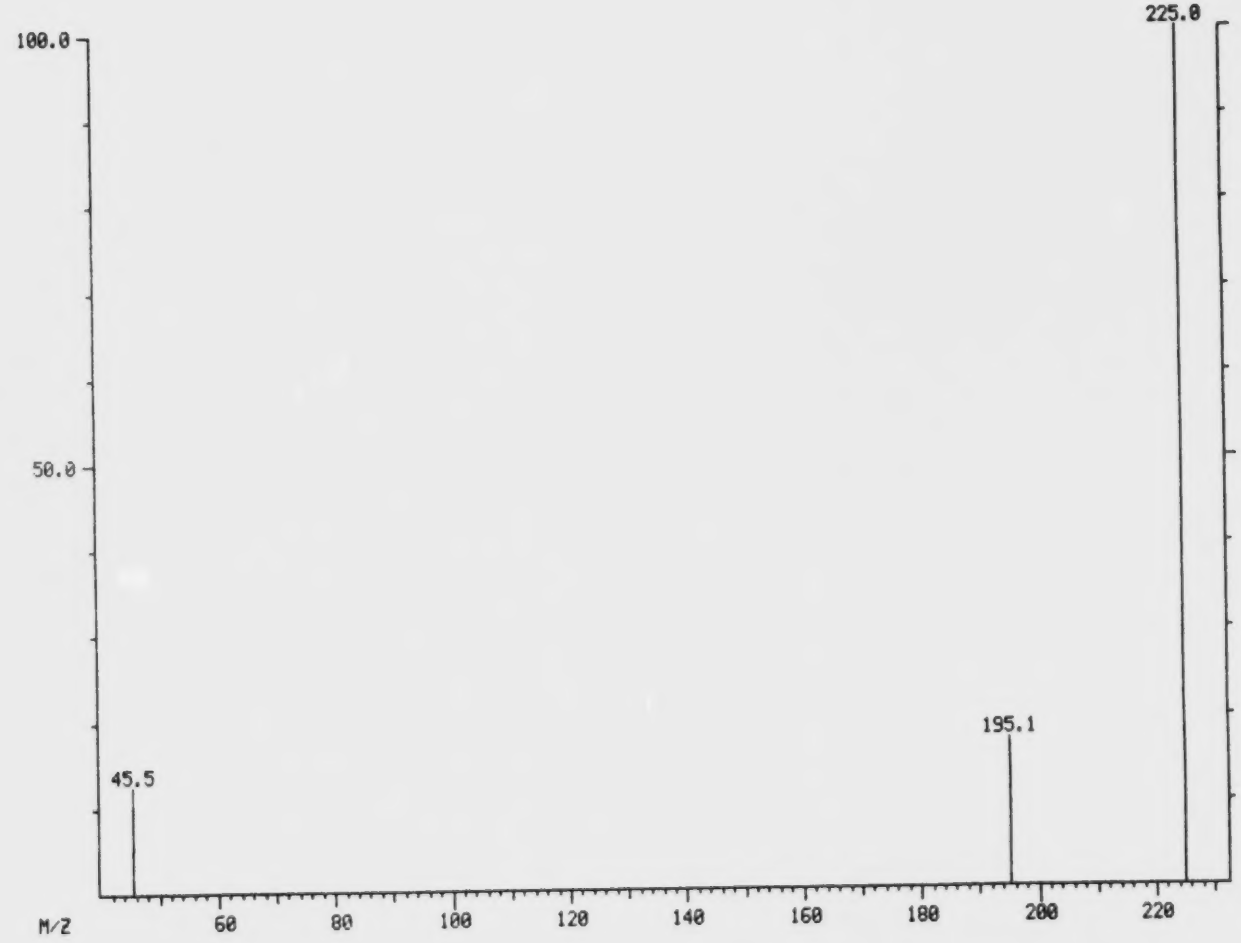

Figure A-5. The NCI daughter spectrum of 3-nitro-9-fluorenone, m/z 225

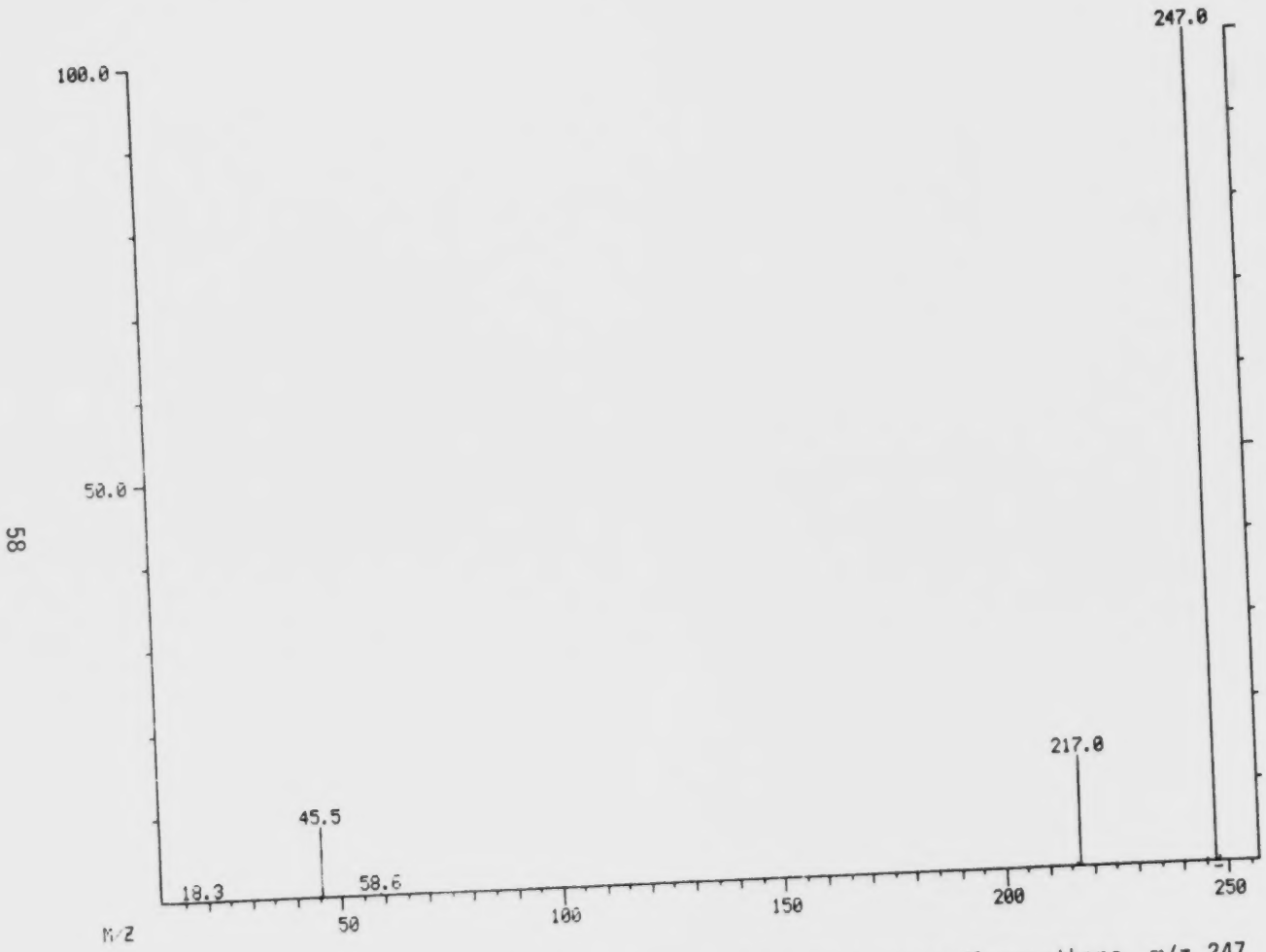

Figure A-6. The NCI daughter spectrum of 3 nitro-fluoranthene, m/z 247

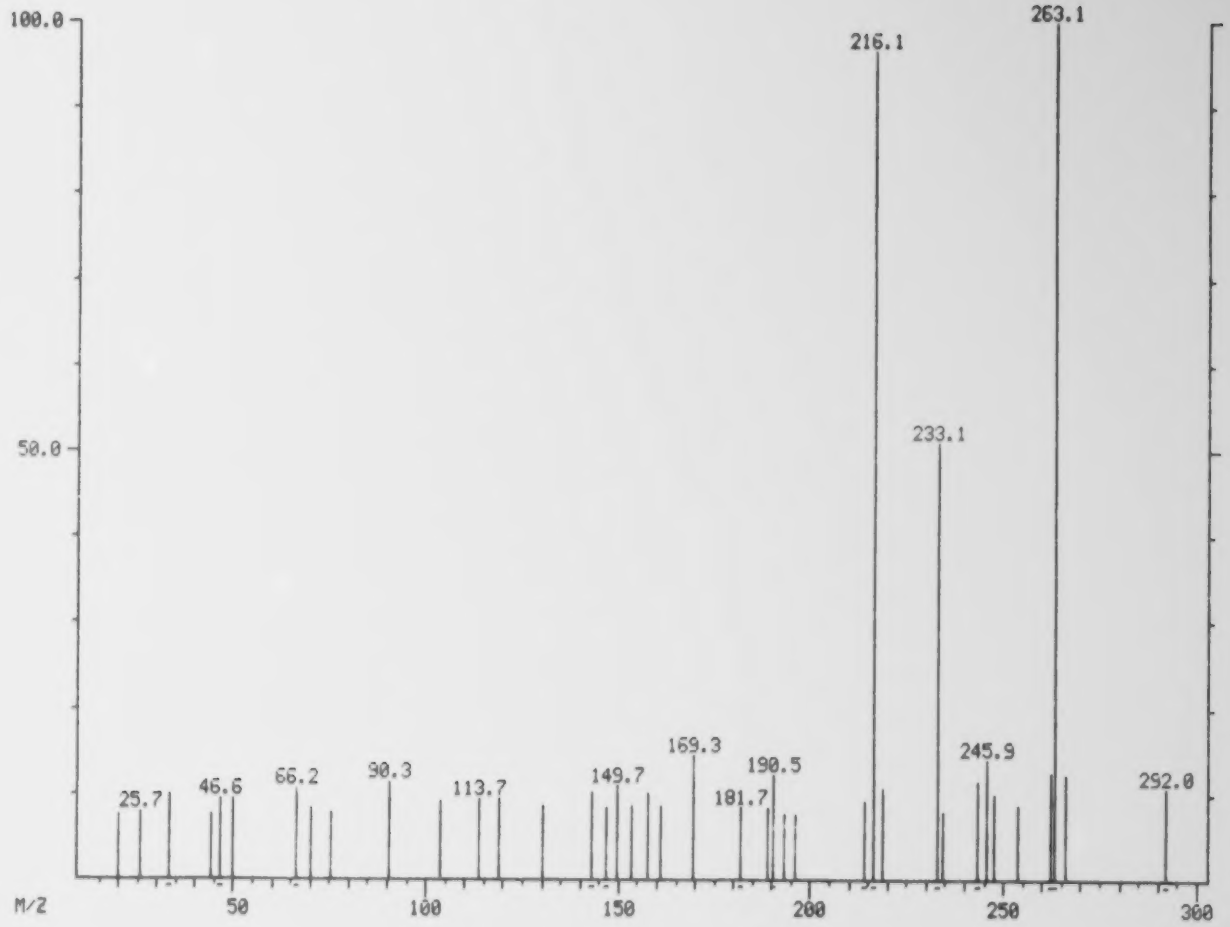

Figure A-7. The NCI daughter spectrum of 4-hydroxynitropyrene, m/z 263

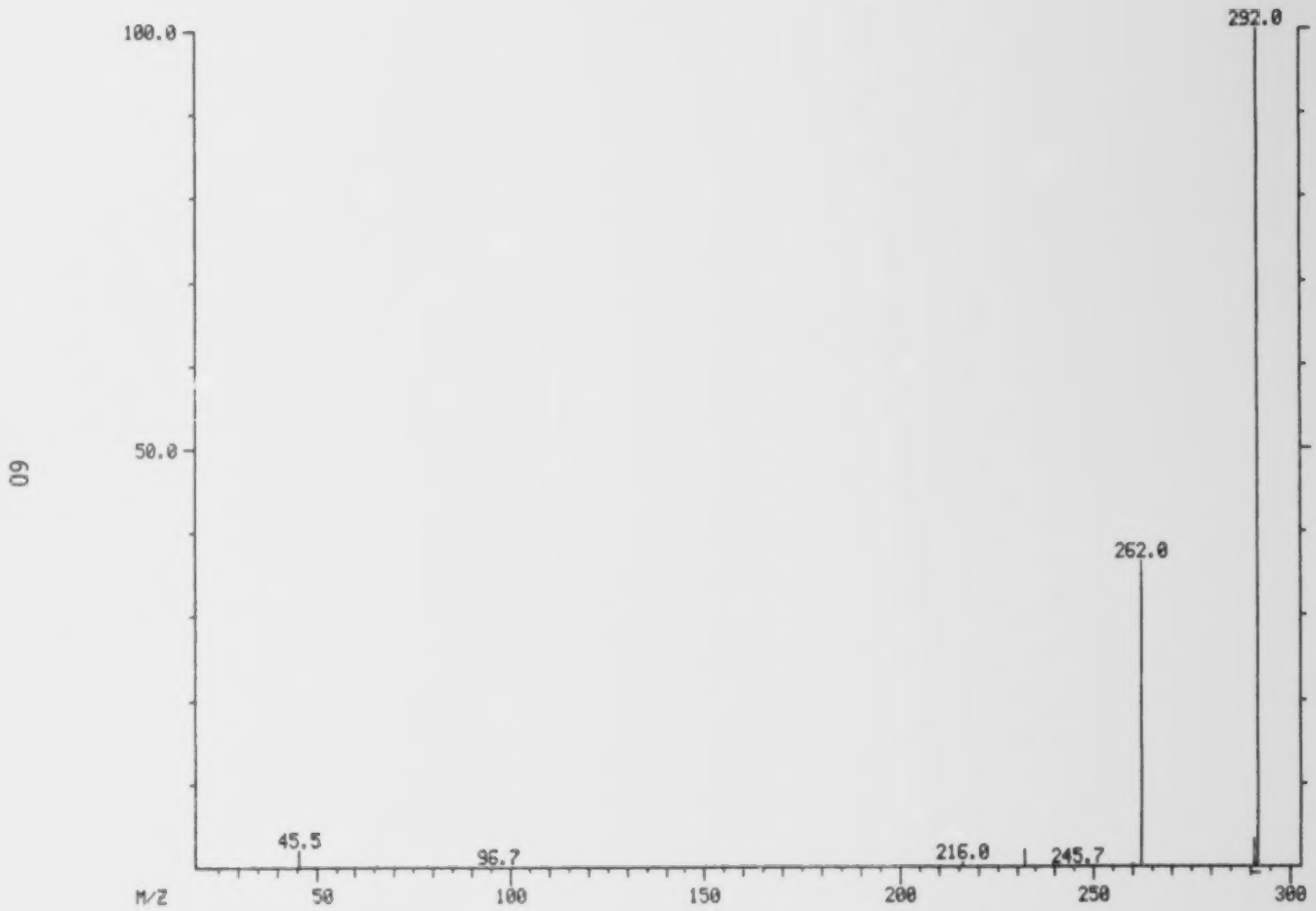

Figure A-8. The NCI daughter spectrum of 1,6-dinitropyrene, m/z 292

APPENDIX B

THE PCI DAUGHTER SPECTRA OF OXYGENATED PAH

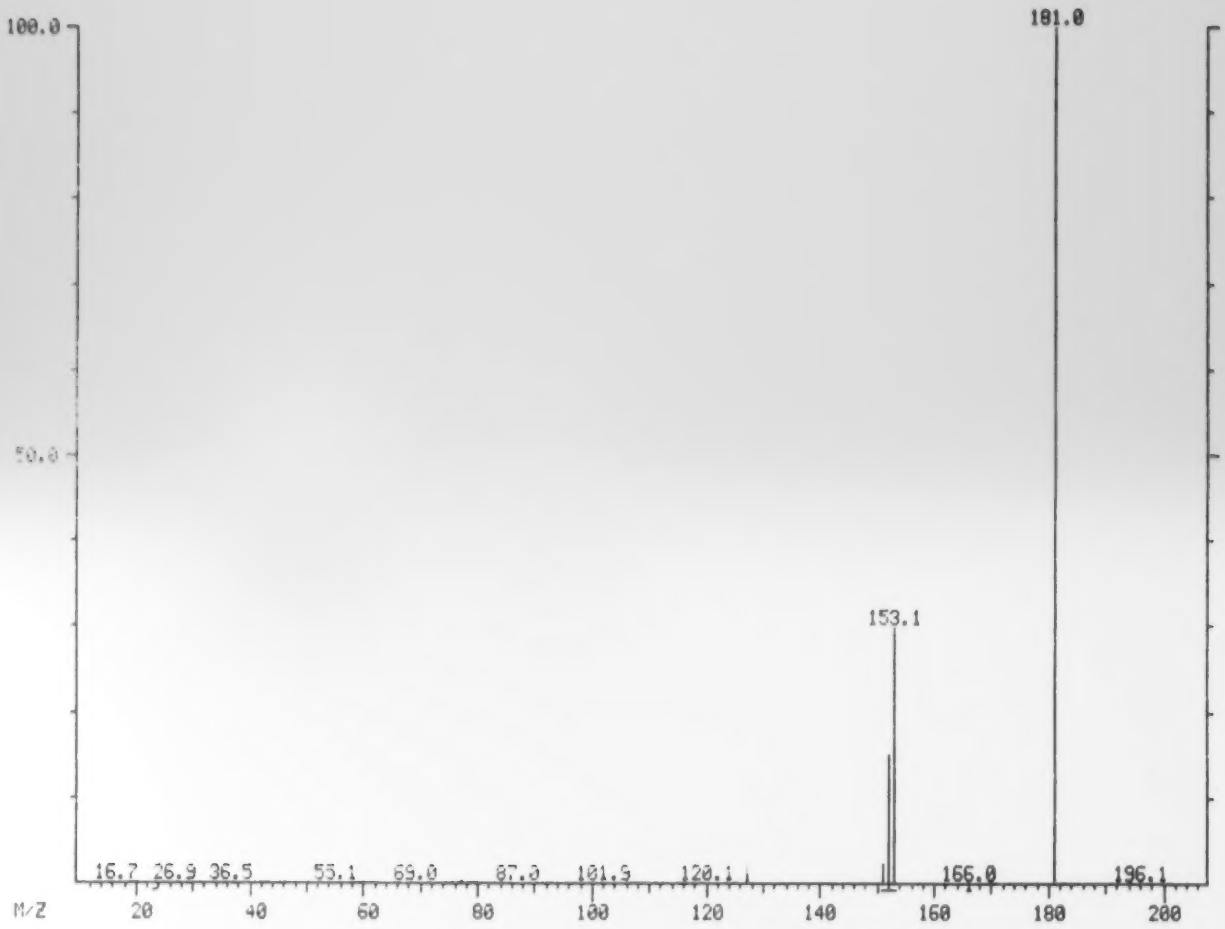

Figure B-1. The PCI daughter spectrum of 9-fluorenone, m/z 180

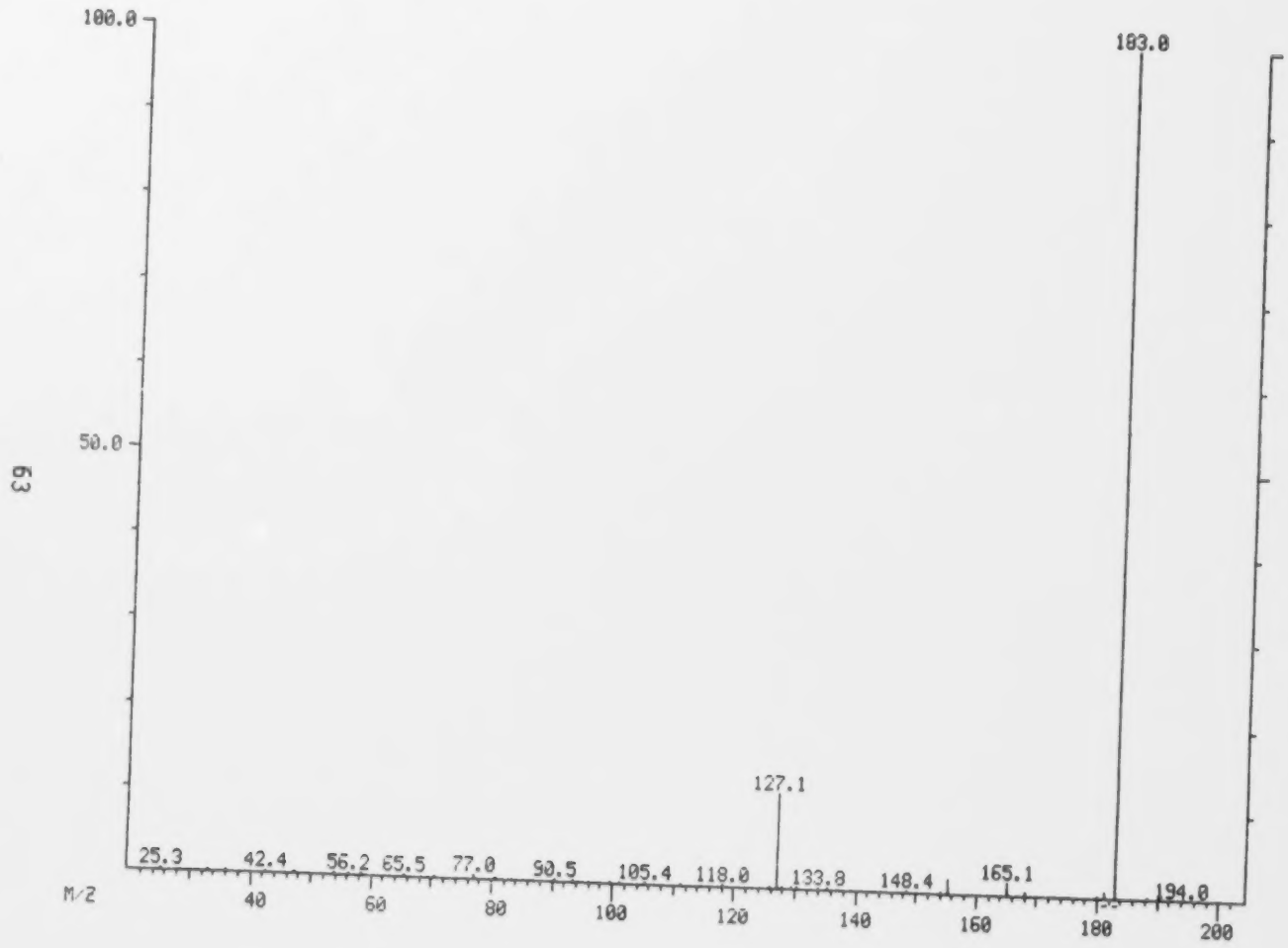

Figure B-2. The PCI daughter of acenaphthylene quinone, m/z 182

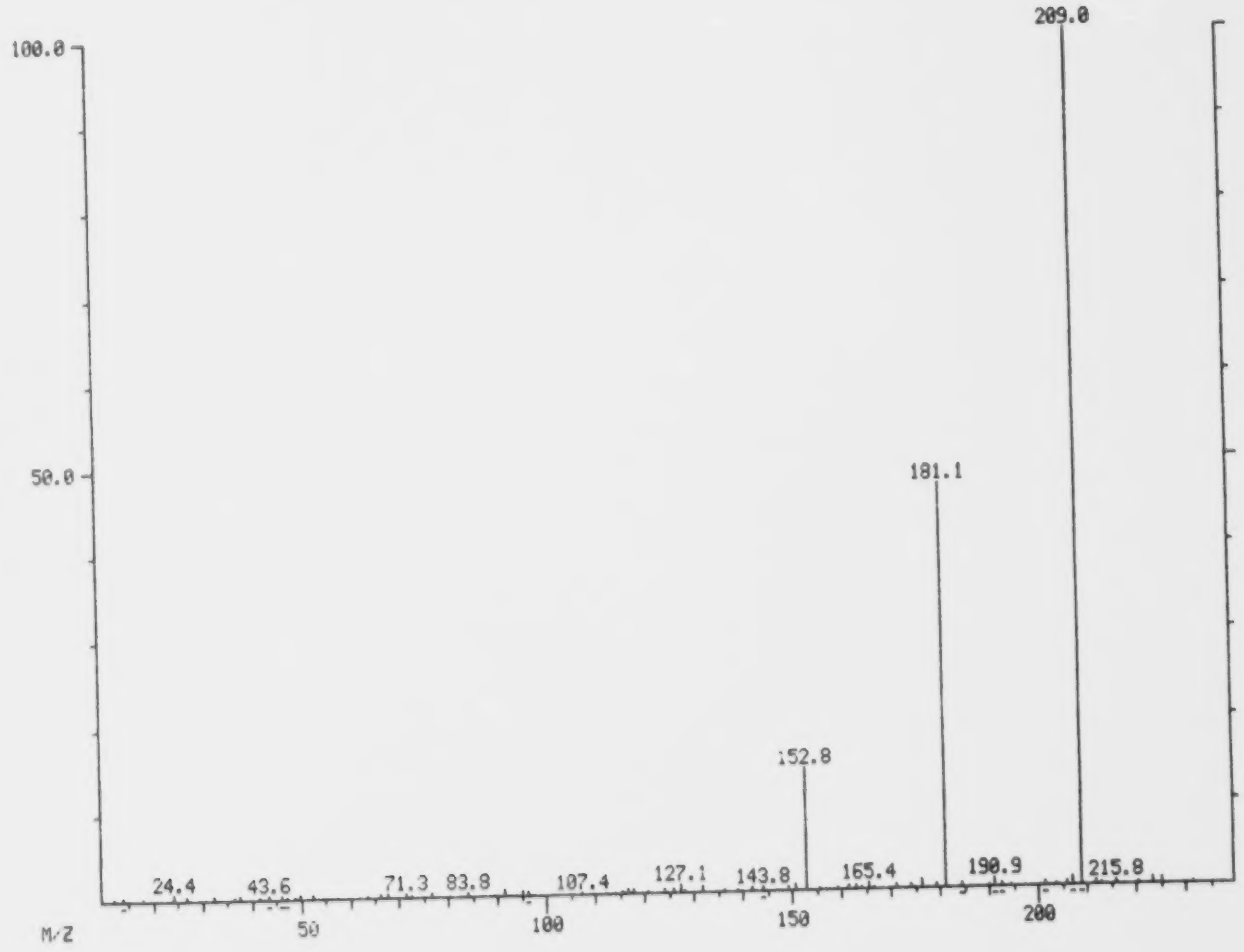

Figure B-3. The PCI daughter spectrum of phenanthrenedione, m/z 208

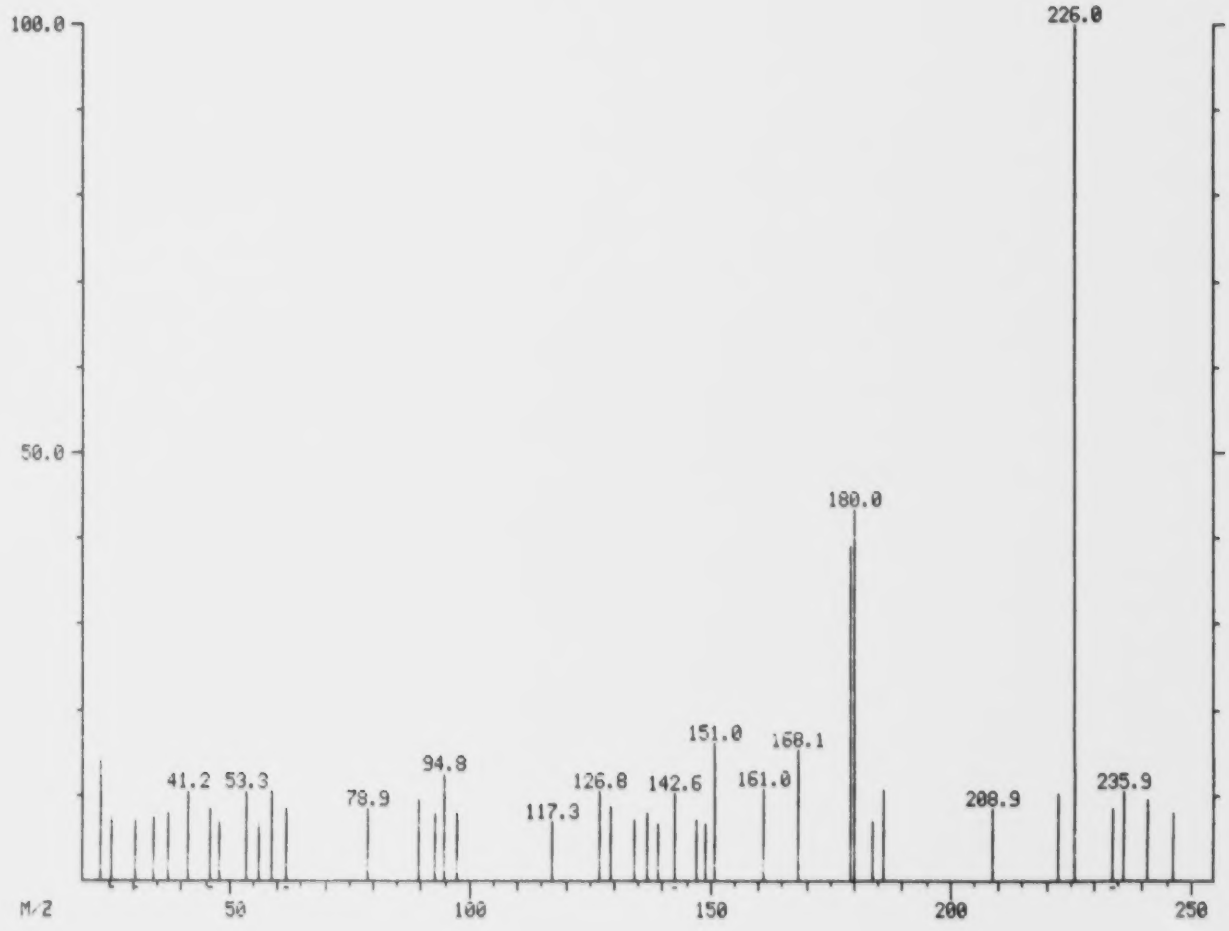

Figure B-4. The PCI daughter spectrum of 3-nitro-9-fluorenone, m/z 225

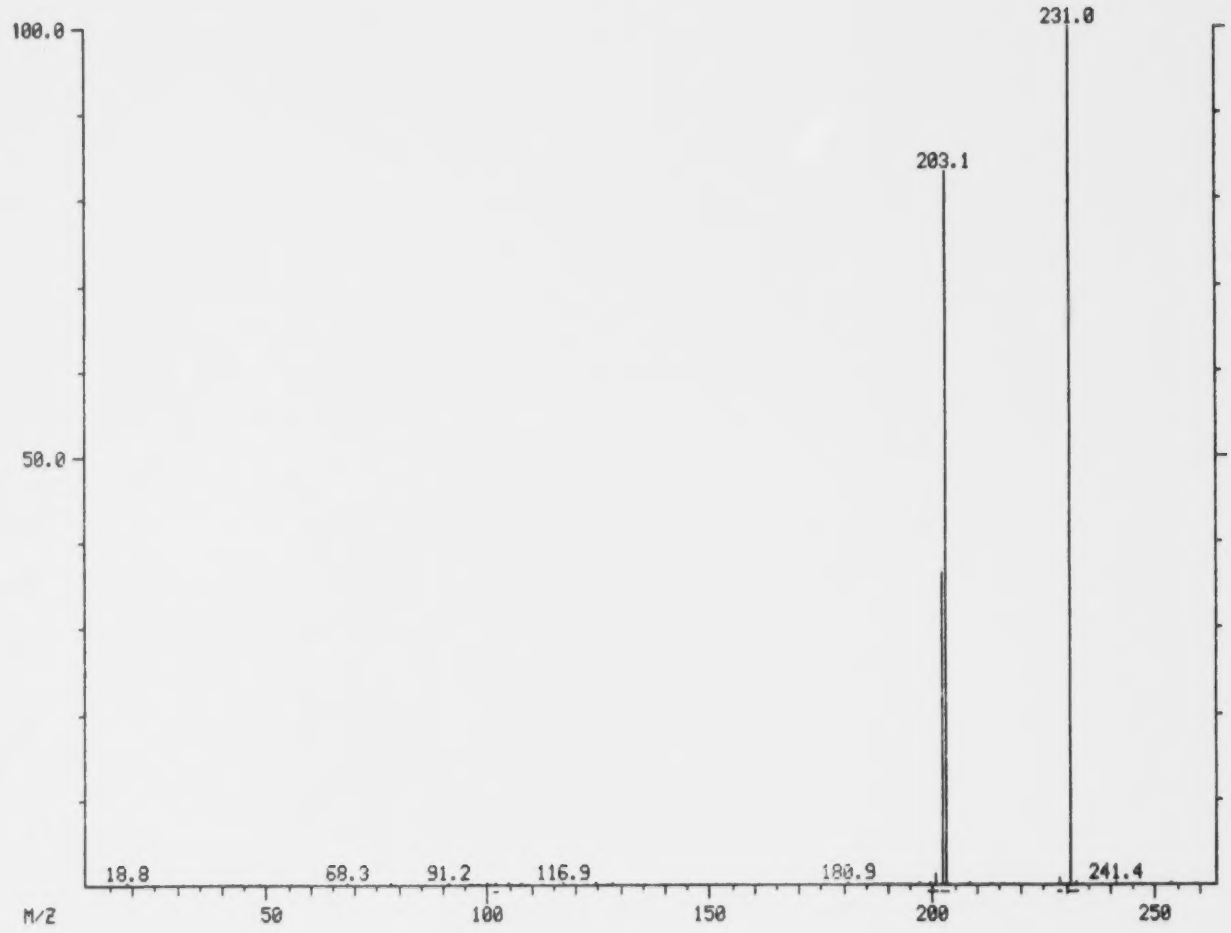

Figure B-5. The PCI daughter spectrum of pyrenecarboxaldehyde, m/z 230

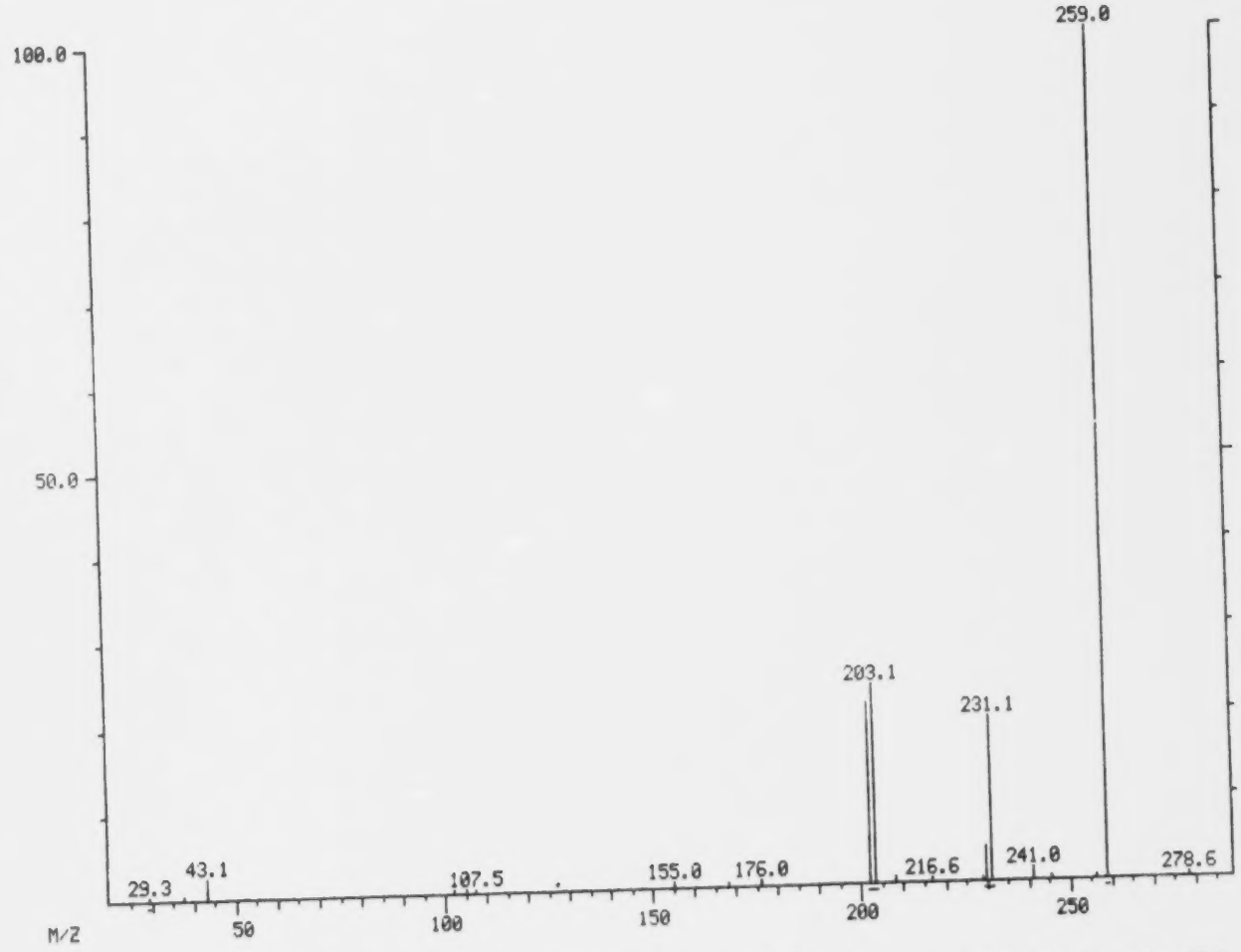

Figure B-6. The PCI daughter spectrum of benz[a]anthracene-7,12-dione, m/z 258